

the one obtained by us for testosterone. Any adsorption data for proteins, which follow the Freundlich isotherm, when  $n = 1$ , and the simple Langmuir equation, would give this result with the Scatchard treatment. The conclusion therefore to be reached is that in the case of a neutral molecule like testosterone the adsorption by albumin is quite non-specific.

A summary of our solubility studies indicates that testosterone added to water and equilibrated for a comparatively short period of time produces a supersaturated solution; the maximum amount is dissolved in about 5 hours. After this peak there is a slow fall to the solubility value,  $1.26 \times 10^{-4}$  mole/l., provided some solid phase is present. If no solid phase is present solutions as concentrated as  $2.05 \times 10^{-4}$  mole/l. can be maintained without crystallization for weeks. If the solvent is changed after 5 hours of equilibration, the residue does not again produce a supersaturated solution. Heating the residue to slightly below the melting point restores the form of material required to produce a supersaturated solution.

According to the Gibbs concept of solubility, solubility is dependent on particle size and the energy of the solvent-solute interface; the final equilibrium is attained with a single large crystal.<sup>14</sup> A number of observations in our experiments would support this hypothesis as an explanation of the dual solubility values obtained: (1) The smaller

(14) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publ. Corp., New York, N. Y., 1943, p. 51.

particles would dissolve rapidly giving an initial high solubility; (2) the residue consisting of larger particles would give the lower equilibrium value; (3) heating crystals, which gave the lower solubility, shatters them and produces a product giving the high solubility; and (4) the high solubility in the water phase of the dialysis experiments, in which the solid phase size may be looked upon as the albumin molecule upon which the testosterone is adsorbed. Attractive as these arguments may appear, actual measurement of particle size by microscopic examination showed particles of from 1 to 10 microns in the low solubility solute, as well as in the high. A quantitative estimate of the distribution of particle size was not made, so that the Gibbs theorem cannot be completely ruled out. The only other explanation would be the existence of polymorphous forms of testosterone. In either case, regardless of the interpretation, the albumin increases the fugacity of testosterone in the water phase, a phenomenon which may have biologic implications.

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## Molecular Structures of *trans*-1,2-Dihalocyclohexanes

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An investigation of dipole moments and Raman spectra of the addition products of chlorine or bromine to cyclohexene leads to the following conclusions: (1) the compounds are *trans*-1,2-dihalocyclohexanes; (2) their solutions or melts contain the two inverted isomers (1p, 2p)  $\rightleftharpoons$  (1e, 2e) in a dynamic equilibrium; (3) the structure (1e, 2e) is more stable in dilute benzene solution than in dilute heptane or carbon tetrachloride solution; and (4) in the solid state the dichloro derivative exists only in the (1e, 2e) form, but the dibromo derivative exists only in the (1p, 2p) form. The potential energy differences of both structures were estimated for various dilute solutions of *trans*-1,2-dichlorocyclohexane and of *trans*-1,2-dibromocyclohexane.

The possible existence of *cis-trans* isomers of 1,2-dihalocyclohexanes which has been assumed for several decades by organic chemists has in recent years also been suggested on the basis of structural considerations of the cyclohexane ring of  $D_{3d}$  symmetry.

Only one isomer, however, is obtained by adding chlorine or bromine to cyclohexene. The compound prepared from bromine and cyclohexene is according to Rothstein<sup>1</sup> the *cis* isomer, while according to Mousseron and Granger<sup>2</sup> the addition of chlorine or bromine to cyclohexene leads to the *trans* isomer.

It is highly probable that the *trans*-1,2-dihalo derivatives, like the *trans*-1,4-dihalocyclohexanes,<sup>3</sup> possess two structures in which the valency angles

of the carbon atoms of the cyclohexane ring maintain their normal value. These two stable strainless structures, the "inverted isomers"<sup>8</sup> of the *trans*-1,2-dihalocyclohexanes, are represented by the symbols (1p, 2p) and (1e, 2e) and should be in dynamic equilibrium, provided the energy difference between the inverted isomers is not too large. For the *cis*-1,2-dihalocyclohexanes the two stable strainless structures (1e, 2p) and (1p, 2e) are identical and therefore only one isomer can be expected.

This difference between *cis* and *trans* isomers, in connection with measurements of Raman spectra and dipole moments, has enabled us to determine whether the actual compounds are *cis* or *trans* isomers, and to study the equilibrium of the inverted isomers in solution.

Recently, Bastiansen and Hassel<sup>4</sup> concluded from

(1) B. Rothstein, *Ann. chim.*, **14**, 461 (1930).

(2) M. Mousseron and R. Granger, *Compt. rend.*, **205**, 327 (1937).

(3) K. Kozima and T. Yoshiino, *This Journal*, **75**, 166 (1953).

(4) O. Bastiansen and O. Hassel, *Tids. Kjemi, Bergesens Met.*, **8**, 96 (1946).

electron diffraction data that the derivative obtained by adding bromine to cyclohexene is the *trans* isomer, and that the vapor contains 60% of the (1e; 2e) form and 40% of the (1p, 2p) form.

### Experimental

**Preparation and Purification of Compounds.**—Cyclohexene was prepared according to Osterberg and Kendall<sup>5</sup> by the dehydration of cyclohexanol using sulfuric acid; boiling range 82.7–83.0°. Bromine or chlorine was added to cyclohexene in carbon tetrachloride solution at 0 to –10° under scattered light. The products were purified by repeated distillation *in vacuo*; the dichloro derivative boiled at 96.0–96.4° at 45 mm., the dibromo derivative at 85.5–86.0° at 11 mm. Since the boiling points of both products are nearly constant, both seem to be composed of one isomer only as reported before. This result is supported by the Raman spectra.

**Electric Dipole Moments.**—For the measurement of dielectric constants the same instrument was used as before.<sup>3</sup> The data are listed in Table I, where  $f$  denotes the mole fraction and  $P_2$  the molar polarization of the solute. The measured values of  $P_2$  are in various cases almost independent of the low concentrations which were used. Therefore,

TABLE I  
MOLAR POLARIZATIONS

*trans*-1,2-Dichlorocyclohexane in carbon tetrachloride:

$f$	$t = 30^\circ, P_{2\infty} = 131$		$P_2$
	$\epsilon$	$d$	
0.0000	2.213	1.5722	
.01287	2.286	1.5659	130
.01867	2.321	1.5625	132
.02391	2.351	1.5601	130

$f$	$t = 50^\circ, P_{2\infty} = 126$		$P_2$
	$\epsilon$	$d$	
0.0000	2.173	1.5329	
.01287	2.240	1.5271	125
.01867	2.272	1.5240	127
.02391	2.300	1.5224	126

$f$	In benzene: $t = 30^\circ, P_{2\infty} = 165$		$P_2$
	$\epsilon$	$d$	
0.0000	2.262	0.8698	
.01855	2.424	.8776	166
.02267	2.459	.8793	164

$f$	$t = 50^\circ, P_{2\infty} = 156$		$P_2$
	$\epsilon$	$d$	
0.0000	2.220	0.8480	
.01855	2.364	.8560	156
.02267	2.395	.8579	156

*trans*-1,2-Dibromocyclohexane in carbon tetrachloride:

$f$	$t = 10^\circ, P_{2\infty} = 107$		$P_2$
	$\epsilon$	$d$	
0.0000	2.253	1.6142	
.01076	2.2994	1.6172	107
.01703	2.3250	1.6189	106
.02222	2.349	1.6203	107

$f$	$t = 25^\circ, P_{2\infty} = 106$		$P_2$
	$\epsilon$	$d$	
0.0000	2.225	1.5850	
.01076	2.2695	1.5882	106
.01703	2.2959	1.5902	106
.02222	2.319	1.5917	107

$f$	$t = 40^\circ, P_{2\infty} = 105$		$P_2$
	$\epsilon$	$d$	
0.0000	2.197	1.5560	
.01076	2.2385	1.5592	104
.01703	2.2639	1.5611	105
.02222	2.285	1.5624	105

(5) A. E. Osterberg and E. C. Kendall, *THIS JOURNAL*, **42**, 2620 (1920).

$f$	In <i>n</i> -heptane: $t = 10^\circ, P_{2\infty} = 108$		$P_2$
	$\epsilon$	$d$	
0.0000	1.935	0.6929	
.01374	1.9727	.7073	107
.01884	1.9880	.7129	108
.02381	2.0014	.7178	108

$f$	$t = 30^\circ, P_{2\infty} = 107$		$P_2$
	$\epsilon$	$d$	
0.0000	1.904	0.6758	
.01374	1.9402	.6899	107
.01884	1.9551	.6955	108
.02381	1.9679	.7004	107

$f$	$t = 50^\circ, P_{2\infty} = 106$		$P_2$
	$\epsilon$	$d$	
0.0000	1.873	0.6584	
.01374	1.9079	.6725	106
.01884	1.9219	.6779	107
.02381	1.9341	.6828	106

$f$	In benzene: $t = 10^\circ, P_{2\infty} = 143$		$P_2$
	$\epsilon$	$d$	
0.0000	2.300	0.8898	
.009029	2.3655	.9024	143
.01434	2.4064	.9098	144

$f$	$t = 30^\circ, P_{2\infty} = 136$		$P_2$
	$\epsilon$	$d$	
0.0000	2.261	0.8682	
.009029	2.3190	.8807	135
.01434	2.3557	.8878	137

$f$	$t = 50^\circ, P_{2\infty} = 131$		$P_2$
	$\epsilon$	$d$	
0.0000	2.221	0.8467	
.009029	2.2749	.8593	131
.01434	2.3075	.8663	132

the mean value of  $P_2$  was taken as  $P_{2\infty}$  in all cases. The dipole moment was calculated as  $\mu = 0.0127 \sqrt{(P_{2\infty} - R_D)T}$  using the molecular refraction  $R_D$  calculated from the atomic refractions for the *n*-line; 37.5 cc. for the dichloro derivative, and 43 cc. for the dibromo derivative.

The values of the electric moments are listed in Table II, together with values calculated as explained below.

TABLE II

### DIPOLE MOMENTS

*trans*-1,2-Dichlorocyclohexane

$t, ^\circ\text{C.}$	Carbon tetrachloride soln.		Benzene soln.	
	$\mu_{\text{obs.}}$	$\mu_{\text{calc.}}^{\Delta E = 50}$ cal./mole	$\mu_{\text{obs.}}$	$\mu_{\text{calc.}}^{\Delta E = 400}$ cal./mole
30	2.15	2.16	2.52	2.53
50	2.16	2.17	2.50	2.51

*trans*-1,2-Dibromocyclohexane

$t, ^\circ\text{C.}$	Carbon tetrachloride soln.		Benzene soln.		<i>n</i> -Heptane soln. $\mu_{\text{obs.}}$
	$\mu_{\text{obs.}}$	$\mu_{\text{calc.}}^{\Delta E = 500}$ cal./mole	$\mu_{\text{obs.}}$	$\mu_{\text{calc.}}^{\Delta E = 80}$ cal./mole	
10	1.71	1.70	2.14	2.13	1.72
25	1.74	1.73			
30			2.13	2.14	1.77
40	1.77	1.76			
50			2.14	2.14	1.81

**Raman Spectra.**—The same spectrograph was used as in our earlier work.<sup>3</sup> Because of the color of the dibromo derivative, saturated sodium nitrite solution was used as a filter. The observation tube consisted of two concentric glass jackets; running water was passed through the outer jacket for cooling; the other jacket contained the filter. The spectra of both compounds were observed for the solid and liquid states and for various solutions. The results of wave number readings are shown in Tables III, IV and V, together with the visually estimated relative intensities.

TABLE III

RAMAN SPECTRA OF *trans*-1,2-DICHLOROCYCLOHEXANE<sup>6</sup> IN CM.<sup>-1</sup>

Liquid	Solid	Liquid	Solid
184(3)	—	947(0)	
233(2)		980(2)	979(2)
284(2)		1040(2b)	
305(5)		1050(2b)	1050(2b)
337(1)	338(0)	1104(1)	1105(0)
370(3)		1146(0)	
383(9)	381(6)	1205(2b)	1203(2)
445(3)	443(2)	1271(3)	
500(3)		1283(2)	1281(2)
511(2)		1344(4b)	1341(3b)
619(0)		1382(3b)	
700(7b)		1433(2)	
738(7b)	737(5b)	1448(5)	1444(3)
807(3)			
826(3)		2865(9b)	—
846(2)	847(1)	2905(5bb)	2940(3b)
870(1)		2955(10bb)	2960(3b)
910(1)	910(0)	2985(6bb)	

TABLE IV

RELATIVE INTENSITIES OF RAMAN LINES OF *trans*-1,2-DICHLOROCYCLOHEXANE<sup>7</sup>

CM. <sup>-1</sup>	Pure liquid	CCl <sub>4</sub> soln.	n-Heptane soln.	Benzene soln.	Solid	Configuration
383	9	3	1	2	6	e,e
445	3	—	—	0	2	e,e
500	3	1	0	—		p,p
700	7b	5	3	1		p,p
738	7b	1	0	1	5b	e,e
807	3	*	*	*		p,p?
826	3	2	*	—		p,p
1271	3	2	1	—		p,p
1448	5	2b	*	—	3	e,e

The spectra of both compounds (liquid phase) obtained by Canals, *et al.*,<sup>8</sup> which are very incomplete, and of the dibromide reported by Kohlrausch, *et al.*,<sup>9</sup> agree, within the accuracy of the measurements, with our data for the strong lines, except the doublets at 685 and 699 cm.<sup>-1</sup>. However, our observations include some additional lines.

Only the data for the pure liquids are given in Tables III and V, because the wave numbers of the spectra of both compounds in solution do not differ from those for the pure liquids. The relative intensities, however, vary with the solvent. For the dichloro derivative this is shown by the data for the stronger lines listed in Table IV. The concentration of the solutions was 7 mole per cent. The solvent effect on the relative intensities is less pronounced for the dibromo derivative, but observation by means of the microphotometer showed that the lines marked with + in Table V are stronger for methanol solution than without solvent.

As in the case of the *trans*-1,4-dihalocyclohexanes about half of the lines of the liquid spectra are absent in the spectra of the solids.

(6) Since the spectra of the solids were observed using a filter, the exciting line was only the e-line. Consequently, the Raman lines marked with (—) in Tables III and V are uncertain because of overlapping with the Hg-lines.

(7) Raman lines marked with (\*) are uncertain because of overlapping with the intense Raman lines of the solvents; those marked with (—) do not appear in the spectrum due to the dilute solutions used in the measurements.

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

(9) K. W. F. Kohlrausch, A. Pongratz and R. Seka, *Monatsh.*, **70**, 213 (1937).

TABLE V

RAMAN SPECTRA OF *trans*-1,2-DIBROMOCYCLOHEXANE IN CM.<sup>-1</sup>

Liquid	Solid	Con-figuration	Liquid	Solid	Con-figuration
	101(2)	p,p	972(2)		e,e
142(2)	144(4)	p,p	1003(0)		
	168(2)	p,p	1029(4)	1026(2)	p,p
178(8)	178(7)	p,p	1058(1)	1060(0)	p,p
220(2)+		e,e	1201(6)	1194(6)	p,p
236(7)	236(6)	p,p	1255(4)	1254(2)	p,p
307(8)+		e,e	1270(2)	1265(0)	p,p
322(0)	326(00)	p,p	1279(0)		
340(1)		e,e	1297(2)		e,e
363(1)	359(1)	p,p	1330(1)		e,e
476(7)	475(6)	p,p	1429(3)	1431(1)	p,p
538(3)		e,e	1449(3)		e,e
651(25)	647(20)	p,p			
685(3)+		e,e			
699(3)+		e,e			
803(6)	810(7)	p,p			
812(6)+		e,e	2865(6b)	—	
839(0)	840(00)	p,p	2903(4b)		
867(5)	864(4)	p,p	2946(7b)	2949(3b)	
903(0)			2987(4b)	2988(2b)	

### Discussion of Results

Of the two inverted isomers of the *trans*-1,2-dihalocyclohexanes, (1p, 2p) and (1e, 2e), the former should have nearly a zero dipole moment, while the latter should have a moment of about the same magnitude as the gauche-form of a 1,2-dihaloethane. Therefore, if the abundance ratio of these inverted isomers varies with temperature or solvent, the dipole moment should vary correspondingly. On the other hand, since *cis*-1,2-dihalides can exist in one form only, the moments of these isomers should not vary with temperature or solvent.

The dipole moment of 1,2-dichlorocyclohexane does not vary within the temperature range investigated, but there is a marked difference between the moments measured in carbon tetrachloride and in benzene. The dipole moment of 1,2-dibromocyclohexane in heptane shows a marked change with temperature and again the moment varies considerably between carbon tetrachloride and heptane on the one hand, and benzene on the other. Because of the variations of dipole moment, both compounds must be the *trans* isomers.

The same conclusion is drawn from the Raman spectra. The relatively strong lines of the liquid spectra of both 1,2-dihalocyclohexanes listed in Tables III and V can be divided into two groups, according to whether or not the lines persist in the spectra of the solids. This behavior can be explained if one group of the Raman lines is due to one and the other group is due to the other of the two configurations of the *trans* isomer. No such phenomenon could be expected for the *cis* isomers.

Since both of the compounds are *trans* isomers, the addition of chlorine and of bromine to cyclohexene proceeds as a "*trans* addition."

It seemed to be of considerable interest to determine which of the two inverted isomers predominates in solution and exists exclusively in the solid. To answer the first problem, let us consider the

value of the moment for the *trans* isomer. If the moment of the (1p, 2p) form is  $\mu_p$  and that of the (1e, 2e) form is  $\mu_e$ , the moment  $\mu$  of the *trans* isomer is represented by equation 1

$$\mu^2 = (N_e\mu_e^2 + N_p\mu_p^2)/(N_e + N_p) \quad (1)$$

where  $N_e$  and  $N_p$  are the numbers of molecules in the (1e, 2e) or the (1p, 2p) forms, respectively. Furthermore, it is evident that the abundance ratio  $r$ , *i.e.*,  $N_e/N_p$ , is given by equation 2

$$r = N_e/N_p = (f_e/f_p) \exp. (-\Delta E/RT) \quad (2)$$

where  $f_e$  and  $f_p$  are, respectively, the partition function of each of the structures shown by the suffixes,  $\Delta E$  is the difference between the potential energies ( $E_e$ ) of the (1e, 2e) form and ( $E_p$ ) of the (1p, 2p) form ( $\Delta E = E_e - E_p$ ). By combining 1 and 2, and on the assumption that the relation  $f_e = f_p$  is approximately satisfied in this case, we obtain equation 3

$$\mu^2 = \{\mu_p^2 \exp. (\Delta E/RT) + \mu_e^2\}/\{1 + \exp. (\Delta E/RT)\} \quad (3)$$

From equation 2 we can see that the temperature dependence of the abundance ratio  $dr/dT$ , is zero when  $\Delta E$  is zero or has a value greater than  $RT$ , and that  $dr/dT$  reaches a maximum between these two values of  $\Delta E$ . Consequently, the two values of  $\Delta E$  for the given values of  $\mu_p$  and  $\mu_e$  should show the same variation of the moment with temperature. Of the two values of  $\Delta E$ , which show the observed dependence of the moment on temperature, however, only one of the two values gives the observed values of the moment.

Because of the so-called "inductive effect" the value of  $\mu_p$  may be slightly different from zero, although this neglect does not seriously affect the conclusions to be mentioned below. Therefore, we may take the value of  $\mu_p$  of both compounds to be  $0.4D$ . By use of equation 3 and the above values of  $\mu_p$ , we can then determine the values of  $\Delta E$  and  $\mu_e$ , so that the calculated values agree with the measured values of the temperature dependence of the moment and also with those of the moment.

For the dibromo derivative in the dilute carbon tetrachloride solution, the values obtained for  $\Delta E$  and  $\mu_e$  are 500 cal./mole and  $3.10D$ , respectively. The moments obtained with these values are shown in Table II as  $\mu_{\text{calc.}}$ . As the values of  $\mu_e$  and  $\mu_p$  should hardly vary with the solvent, the same values may be used for calculating the moments for the other solution. Thus, the value of  $\Delta E$  in the dilute benzene solution is obtained as 80 cal./mole. The calculated values of the moments of *trans*-1,2-dibromocyclohexane in Table II are in good agreement with the observed values. Since the moments in the dilute heptane solution do not considerably differ from those in carbon tetrachloride,  $\Delta E$  has almost the same value in both solvents.

The values of  $\mu_e$  and  $\mu_p$  of the dichloro derivative should not differ very much from those of the dibromo derivative. We use, therefore, the same values of  $\mu_e$  and  $\mu_p$  as for the dibromo derivative and determine the values of  $\Delta E$  to be 50 cal./mole in the dilute carbon tetrachloride solution and  $-400$  cal./mole in the dilute benzene solution in order to obtain a close fit between observed and calculated

values. The uncertainty in the estimated values of  $\mu_e$  and  $\mu_p$  does not seriously affect the values of  $\Delta E$ . It is interesting that the differences between  $\Delta E$  in carbon tetrachloride and in benzene are about 450 cal./mole for both the chloro and bromo compounds.

From the foregoing we can see that the (1p, 2p) forms for both compounds are more stable than (1e, 2e) forms, except in the case of the benzene solution of the dichloro derivative. Comparison of the energy difference between the two forms of both compounds in the same solvents shows that the (1e, 2e) forms of the dibromo derivative are less stable than of the dichloro derivative. This effect may be caused by the larger van der Waals radius of bromine atom than chlorine atom.

A new 1,2-dichlorocyclohexane, presumably the *cis* isomer, has recently been described by Carroll, *et al.*,<sup>10</sup> and by Stevens, *et al.*<sup>11</sup> According to our preliminary measurements<sup>12</sup> the new compound has a dipole moment of about  $3.1D$  in carbon tetrachloride. This result and Raman measurements show that it is undoubtedly the *cis* isomer. In agreement with the expectation that the moment of the (1p, 2e) form of the *cis* isomer should hardly differ from that of the (1e, 2e) form of the *trans* isomer observed moment agrees well with our estimated value for the (1e, 2e) form.

Since one group of the Raman lines of *trans*-1,2-dichlorocyclohexane (Table III) is stronger in benzene than in carbon tetrachloride solution, and the dipole moments show that the (1e, 2e) form is more abundant in benzene than in carbon tetrachloride, we assign to the (1e, 2e) form those Raman lines which are intensified in benzene. The other group of Raman lines belongs, therefore, to the (1p, 2p) form. Since the lines belonging to the (1e, 2e) form persist in the spectrum of the solid this form is present in the solid compound, while the equilibrium  $(1e, 2e) \rightleftharpoons (1p, 2p)$  exists in the liquid state and in solution. The last column in Table IV lists the configurations responsible for the various Raman lines.

The situation is different for the dibromo derivative. According to Mizushima, *et al.*,<sup>13</sup> it is highly probable that the more polar of two interchangeable forms becomes more stable in a solvent of higher dielectric constant, except in the case of benzene. We therefore attribute the Raman lines which are stronger for the methanol solution than for the pure liquid (marked + in Table V) to the more polar (1e, 2e) form. Since the other group of Raman lines persists in the solid spectrum, solid *trans*-1,2-dibromocyclohexane is the (1p, 2p) inverted isomer.

This conclusion is supported by evidence based on the analogy of the Raman spectra of the chloro and the bromo compounds which is caused by their structural similarity; both inverted isomers of both

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(11) H. C. Stevens and O. Grummitt, *ibid.*, **74**, 4876 (1952).

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compounds have the symmetry of the  $C_2$  point group. However, even when considering the skeletal modes of vibration, the vibrational secular determinants (constructed by Wilson's method) are of eighteenth order for each structure, and when one uses the generalized coordinates with the proper symmetry, the determinants are broken up only into the following orders: ten of A and eight of B. It is too tedious, therefore, to solve the secular determinants in order to assign each Raman frequency to each type of the skeletal modes of vibration. Fortunately, however, the characteristic frequencies of the carbon-halogen stretching vibrations appear, as is well known, generally in the definite region of vibrational spectra. Therefore, it seems reasonable that the characteristic frequencies are at 700 and 738  $\text{cm.}^{-1}$  for the dichloro derivative and at 651, 685 and 699  $\text{cm.}^{-1}$  for the dibromo derivative. Since the molecules containing the two carbon-halogen bonds can have both structures in the liquid or solution states and all of the vibrations are active in both the Raman and infrared spectra, the four characteristic frequencies of the carbon-halogen stretching vibrations should appear in the liquid or solution spectra. However, only two of them appear for the dichloro derivative and only three for the dibromo derivative. This deficiency can be explained as follows. With the dichloro derivative one of the two missing characteristic frequencies should be due to the (1p, 2p) form. Since its mode of vibration will be antisymmetric to the symmetry operation  $C_2$  and similar to the antisymmetric vibration of the *trans* form of 1,2-dihaloethane, we may well expect the line to be weak in the Raman spectrum, but strong in the infrared spectrum. The situation may be the same for the one missing frequency of the dibromo derivative. With respect to the other missing line of the dichloro derivative it is highly probable that the line at 738  $\text{cm.}^{-1}$  is a doublet because the line is very broad and seems to correspond to the doublet of the dibromo derivative.

We have recently been able to confirm these considerations by infrared spectra of the pure liquids<sup>14</sup> taken with a Perkin-Elmer infrared spectrophotometer (Model 112) and NaCl and KBr prisms.

The observed characteristic frequencies for the carbon-halogen stretching vibrations are shown in Table VI. For the bands which appeared in both spectra the wave number readings coincide

(14) An article by M. Larnaudie on the infrared spectra of disubstituted cyclohexane recently appeared in *Compt. rend.*, **256**, 909 (1953). Our wave numbers agree closely with his, and his interpretations are not in disagreement with our results so far as *trans*-1,2-dihalo-cyclohexanes are concerned.

TABLE VI  
CHARACTERISTIC FREQUENCIES OF THE CARBON-HALOGEN  
STRETCHING VIBRATIONS OF *trans*-1,2-DIHALOCYCLOHEXANES

Con- figu- ra- tions deter- mined	Dichloro derivative		Dibromo derivative	
	Raman, $\text{cm.}^{-1}$	Infrared, $\text{cm.}^{-1}$	Raman, $\text{cm.}^{-1}$	Infrared, $\text{cm.}^{-1}$
p,p		695.5(s)	651	651(w)
p,p	700			664(vs)
e,e	738	736(s)	685	686(s)
e,e		743(s)	699	697(s)

very well and the observations are in good agreement with the expectation that the line at 738  $\text{cm.}^{-1}$  is a doublet and that for both compounds strong new characteristic bands appear in the infrared spectra. For the two forms of both compounds the two characteristic frequencies which are due to the two normal modes of vibration—symmetric or antisymmetric with respect to the  $C_2$  operation—are very close to each other; for the dichloro derivative the line at 700  $\text{cm.}^{-1}$  did not even resolve into two lines, although the infrared measurements were made in dilute carbon bisulfide. This may be due to the facts mentioned above and indicate that the symmetric vibration of the (1p, 2p) form would be weak in the infrared spectrum, as shown in the case of the dibromo derivative.

Consequently the Raman line at 700  $\text{cm.}^{-1}$  of the dichloro derivative corresponds to the line at 651  $\text{cm.}^{-1}$  of the dibromo derivative, and the line at 738  $\text{cm.}^{-1}$  of the former to the doublets of the latter. In agreement with the assignment of structures and lines for the dichloro derivative, given above, we consider the line at 651  $\text{cm.}^{-1}$  of the *trans*-1,2-dibromocyclohexane as belonging to the (1p, 2p) form and the doublets as belonging to the (1e, 2e) form. Hence, the structure which persists in the crystalline state of the dibromo derivative is the (1p, 2p) form, in good agreement with our conclusions drawn above from different evidence.

It is a noteworthy result of our work, that the molecules of crystalline *trans*-1,2-dichlorocyclohexane have the (1e, 2e) form and the molecules of crystalline *trans*-1,2-dibromocyclohexane are in the (1p, 2p) form.

The intramolecular potentials of these molecules will be discussed in the near future in relation to those of monohalocyclohexanes and 1,2-dihaloethanes.

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