The Molecular Structure of cis-1,2-Dichlorocyclohexane

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(Received March 12, 1954)

1,2-Disubstituted cyclohexanes have two geometrical isomers. One is called the *cis*-isomer and the other the *trans*-isomer. By use of the usual symbols the molecular structure of the former is represented by (le, 2p) or (lp, 2e). As for 1,2-dihalocyclohexanes the *cis*-isomers were not obtained for a long time. However, a new 1,2-dichlorocyclohexane, presumably the *cis*-isomer, has recently been described by Carrol et al.$^{1)}$

If the compound is really *cis*-1,2-dichloro derivative, it should have the following two properties, since its cyclohexane ring should take the chair-form as in the case of the similar derivatives$^{2-4)}$ already reported: (1) The compound has not the "inverted isomer".$^{2-4)}$ (2) The value of dipole moment is nearly the same as that determined by us for the (le, 2e) form of *trans*-1,2-dichloro derivative$^{3)}$, namely 3.1 D.

The main purposes of this research are to ascertain whether or not the compound is the *cis*-isomer by measuring the vibration

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1) B. Carrol, D. G. Kubler, H. W. Davis and A. M. Whaley, *J. Am. Chem. Soc.*, **73**, 5382 (1951).

2) K. Kozima and T. Yoshino, ibid., **75**, 166 (1953).

3) K. Kozima, K. Sakashita and S. Maeda, ibid., **76**, 1965 (1954).

4) K. Kozima, *Bull. Tokyo Inst. Tech.*, **1952**, 1. (in Japanese).

spectra and the dipole moment and, if so, to know the properties of the compound.

Experimental

Preparation and Purification of the Compound.—According to the method of Carrol et al.[1] we prepared the 1,2-dichlorocyclohexane by reacting *trans*-1,2-cyclohexene chlorohydrin with thionyl chloride in the presence of pyridine. The product was purified by the fractional distillation in vacuo. The boiling point is 71.0~71.2° at 8.5 mm.

Electric Dipole Moment.—For the measurement of dielectric constants the same instrument was used as before. 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, the mean value of P_2 was taken as $P_{2\infty}$ in all cases. The dipole moment was calculated as $\mu=0.0128\sqrt{(P_{2\infty}-R_D)\cdot T}$ using the molar refraction R_D (37.5 cc) calculated from the atomic refractions for the D-line.

TABLE I

DIPOLE MOMENTS

in benzene

$t=30°$, $P_{2\infty}=231$, $\mu=3.10$ D.

f	ε	d	P_2
0.0000	2.2625	0.8675	
0.007093	2.3562	0.8709	230
0.008311	2.3738	0.8715	232

in heptane

$t=30°$, $P_{2\infty}=237.5$, $\mu=3.15$ D.

f	ε	d	P_2
0.0000	1.9056	0.6753	
0.01328	2.0026	0.6814	237
0.01492	2.0157	0.6823	238

in heptane

$t=45°$, $P_{2\infty}=225.5$, $\mu=3.13$ D.

f	ε	d	P_2
0.0000	1.8829	0.6625	
0.01328	1.9776	0.6687	225
0.01492	1.9837	0.6696	226

in carbon tetrachloride

$t=40°$, $P_{2\infty}=227$, $\mu=3.12$ D.

f	ε	d	P_2
0.0000	2.1928	1.5563	
0.006699	2.2690	1.5526	227
0.007255	2.2746	1.5519	227

Vibration Spectra.—For Raman spectra the same spectrograph was used as in our earlier work. The spectra of the compound were observed for the solid and liquid states. Regarding infrared spectra measurements were made with Perkin-Elmer spectrometer Model 112 equipped with NaCl and KBr Prisms. The results of the wave number readings for both spectra are shown in Table II.

TABLE II

VIBRATION SPECTRA

Raman* (solid)	Raman* (liquid)	infrared** (liquid)
cm^{-1}	124 (4) cm^{-1}	cm^{-1}
193 (1)	193 (3)	
278 (2)	278 (4)	
348 (10)	346 (10)	
365 (1)	367 (2)	
?	474 (1)	473 (vw)
510 (5)	510 (8)	511 (m)
535 (10)	541 (10)	543 (s)
681 (10)	695 (10)	695 (vs)
735 (9)	741 (9)	741 (vs)
816 (3)	818 (4)	816 (s)
833 (3)	833 (5)	834 (s)
		~845 (vw)sh
876 (2)	876 (4)	877 (vs)
902 (1)	902 (3)	906 (m)
985 (7)	987 (8)	986 (vs)
		~1008 (vw)sh
1026 (2)	1026 (4)	1025 (vw)
1057 (2)	1057 (3)	1057 (w)
1079 (2)	1079 (2br)	1078 (w)
		1085 (w)
?	1133 (1)	1131 (w)
1191 (1/2)	1191 (1)	1191 (m)
1220 (1/2)	1218 (0)	1217 (w)
	1226 (2)	1226 (m)
		~1262 (vw)sh
1267 (3br)	1267 (5br)	1270 (s)
1296 (1/2)	1296 (1)	1298 (m)
?	1314 (1)	1313 (w)
	1335 (1)	1336 (w)
1346 (1br)		~1346 (w)sh
	1355 (1)	1356 (m)
1442 (4br)	1435 (3)	1446 (vs)
	1443 (6)	
		2169 (w)
		2695 (vw)
	2847 (2)	2880 (m)
2903 (3)	2904 (4)	
2920 (3)	2920 (4)	
2941 (4)	2938	2937 (vs)br
2950 (4)	2955 (6br)	
2982 (2)	2977	

* As for the Raman spectra the numbers shown in the brackets are the visually estimated relative intensities.

** The infrared spectra were not investigated below 430 cm.$^{-1}$ The letters shown in the brackets mean the relative intensities. v=very, s=strong, m=medium and w=weak. sh=shoulder.

Discussion

It is seen from Table I that the dipole moment of the compound does not appreciably vary with temperature or solvent. From Table II the following facts may be clear:

(1) The number of the Raman bands and their relative intensities do not vary except for the disappearance of the several very weak lines of the liquid spectrum when the measuring state is changed from liquid to solid. (2) The infrared and Raman spectra agree with each other perfectly regarding the number of the bands and approximately regarding the relative intensities except the very faint bands and the region above 2000 cm^{-1}.

Two possibilities for interpreting the facts mentioned above come out: (1) The molecule does not possess the inverted isomer; or (2) The molecule has the inverted isomer, but the energy difference between the isomers is so great that only one of the two forms can exist. A case in which the energy difference between the isomers is nearly zero or small can be left out of consideration, because of the number of the bands (for instance, the number of the bands assigned to the C—Cl stretching vibrations is two, as might be naturally expected from the formula of $C_6H_{10}Cl_2$).

It is not immediately clear that the dichlorocyclohexane prepared from 1,2-cyclohexene chlorohydrin, as described above, is 1,2-dichlorocyclohexane. Taking this point into consideration these two possibilities will be discussed.

Each of the three position isomers of dichlorocyclohexanes has two geometrical isomers—the *cis*- and *trans*-isomers. Of these six isomers only three have inverted isomers; viz. *trans*-1,2-, *trans*-1,4- and *cis*-1,3-dichlorocyclohexanes. Regarding the first two of them we have already reported[2,3]. Then, only *cis*-1,3-isomer remains to be considered. The structures of *cis*-1,3-dichloro derivative are represented as follows:

$$(1p,\ 3p) \rightleftarrows (1e,\ 3e).$$

The distance between the two chlorine atoms of the (1p, 3p) structure is calculated to be about 2.5 Å, assuming the usual values for the C—C and C—Cl nuclear separations and the tetrahedral valency angle for the carbon atoms of the cyclohexane ring which has the "chair" form. Comparing this distance with twice the van der Waals' radius of the chlorine atom, we can expect that the (1p, 3p) structure will be unstable as compared with the (1e, 3e) structure so that only the latter can exist. Therefore, it is not immediately clear that the compound in question is not *cis*-1,3-dichloro derivative. However, upon the basis of simple vector addition of bond moments, it is calculated that the moment of the (le, 3e) structure of *cis*-1,3-dichloro derivative, $\mu_{1,3}$, and that of *cis*-1,2-dichloro derivative, $\mu_{1,2}$, are represented, respectively, as follows;

$$\mu_{1,3}=2\mu_0\cos\ \theta/2$$
$$\mu_{1,2}=2\mu_0\sin\ \theta/2$$

where μ_0 is the sum of the moment of C—Cl bond and that of C—H bond, and θ is the tetrahedral valency angle of carbon atom. Estimating the value of μ_0 at 1.80 or 1.90 D, we can calculate the values of $\mu_{1,3}$ and $\mu_{1,2}$ obtaining the following results;

$$\mu_{1,3}=2.08 \text{ or } 2.19\ \mathrm{D}$$
$$\mu_{1,2}=2.94 \text{ or } 3.10\ \mathrm{D}$$

The observed value is about 3.1 D which is in good agreement with that obtained by Tulinskie, Di Giacomo and Smyth[5] in the vapor and dilute benzene solution states. The marked difference between the observed value and $\mu_{1,3}$ indicates that the compound is not *cis*-1,3-dichloro derivative. Then we can conclude that the compound is not the isomer which has the inverted isomer.

Next, we must consider the possibility (1). As for the remaining three isomers of dichlorocyclohexanes which do not possess the inverted isomer, it is easily seen that the compound is not *trans*-1,3- or *cis*-1,4-dichloro derivative. The reasons for this* are as follows:

(1) The value of the moment of *trans*-1,3-derivative which has the structure represented by (1e, 3p) or (1p, 3e) should be equal to that of the (1e, 3e) structure of *cis*-1,3-derivative. Consequently, regarding this isomer we cannot expect such a large moment as observed.

(2) The moment of *cis*-1,4-dichloro derivative should be equal to $\mu_{1,2}$ except for a small difference due to the so-called "induction effect". Therefore, we can say that the compound in question may be this isomer so far as the moment is concerned. However, we have already prepared a dichloro derivative as a by-product of the preparation of *trans*-1,4-dichloro derivative, and studied its vibration spectra and other properties. The spectra are quite different from those shown in Table II. We have concluded from such investigations that the compound mentioned above is not *cis*-1,2-dichloro derivative, but is *cis*-1,4-dichloro derivative. Details of this research will be soon described.

Next, we are in a position to discuss whether or not the compound in question is *cis*-1,2-dichloro derivative, which is the only

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[5] A. Tulinskie, A. Di Giacomo and C. P. Smyth, *J. Am. Chem. Soc.*, **75**, 3552, (1953).

* It may not be probable that the compound is the 1,4-dichloro derivative. But we cannot immediately see that it is out of the range of possibility.

isomer* that remains to be considered. Upon the basis of vector addition of bond moment it is expected that the moment of *cis*-1,2-dichloro derivative would be equal to $\mu_{1,2}$ calculated above and to that of the (1e, 2e) structure of *trans*-1,2-dichloro derivative, which we have already estimated at 3.1 D.[3] by the investigations of dipole moments. This value and that of $\mu_{1,2}$ agree with the data shown in Table I. The fact that the Raman and infrared spectra agree with each other indicates that the compound is of low symmetry. For comparison the following fact obtained by us should be noted, namely, regarding the infrared and Raman spectra caused mainly by the C—Cl stretching vibration of the (1p, 2p) isomer of *trans*-1,2-dichloro derivative the mutual exclusion rule for a centrosymmetric molecule holds approximately true, because the molecule has locally the center of symmetry as for the two C—Cl bonds—(the total change of polarizability or dipole moment of the molecule with such normal vibrations as mentioned above may be mainly determined by the change of C—Cl bond polarizabilities or bond moments through the vibrations)—although the molecule as a whole is only of C_2 symmetry. Thus we can, beyond any doubt, conclude that the compound in question is *cis*-1,2-isomer, in conformity with the evidence drawn from the " trans-elimination ".[1]

The authors wish to express their sincere thanks to the Ministry of Education for its financial grant.

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* The possibility that the compound is 1,1-dichloro derivative can be left out of consideration, because the moment of the isomer is expected to be equal to $\mu_{1,3}$ calculated above.