# *Rotational Isomers of Vinyl Ethers. Studies of the Vibrational Spectra and Dipole Moments of cis- and trans-β-Chlorovinyl Methyl Ethers*

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In the course of organic studies for the synthesis of β-chlorovinyl methyl ether in our laboratory, two kinds of compounds with the same chemical composition, $C_3H_5OCl$, were obtained. The first was distilled out at 85～86°C, and the second, at 105～106°C. These two compounds were considered to be the *trans-* and *cis-*β-chlorovinyl methyl ethers. Though the one having the lower boiling point has been supposed to be the trans compound and the other the cis compound, no real evidence has been given for deciding which is the cis or the trans compound. This study was initiated with the aim of identifying the cis and trans compounds in the light of the structural chemistry. First the infrared spectra of these compounds were recorded. The results, however, were not simple enough to enable us to decide confidently which was the cis or the trans compound. Especially, the spectrum of the compound having the lower boiling point proved complex. It seemed to be difficult to explain the complexity of the spectrum in the usual ways, and to be necessary for us to take internal rotation into account. In order to make clear the cis-trans isomerism, the dipole moments were also measured. As the result of these experiments, not only has the compound having the lower boiling point been identified with the trans compound and the other with the cis compound, but also some interesting imformation in connection with the rotational isomerism have been obtained.

The vinyl ether, $CH_2{=}CH{-}O{-}R$, has a freedom of internal rotation about the axis of the C–O bond adjacent to the double bond.

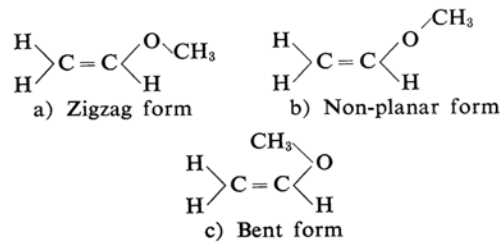



Fig. 1. Rotational isomers of vinyl ether.

Therefore, three types of spacial configuration are possible with regard to the position of alkyl group R: i. e., the zigzag, non-planar and bent forms, which are indicated in Fig. 1.

In a previous study[1] the infrared spectra of several vinyl ethers were investigated, and the observed spectra were assigned in conformity with the assumption that the molecule had the zigzag (planar) configuration. Davison and Bates[2] investigated the infrared spectra of several vinyl ethers and discussed some of the characteristic absorption bands. Kirrman and Chancel[3] also published an elaborate study of the Raman and infrared spectra of vinyl ethers, paying particular attention to the doublets which appeared around 1630 $cm^{-1}$ in most of the spectra investigated, and suggested that the doublets were due to rotational isomers. Since the doublets can also be explained in terms of Fermi resonance[1], uncertainty about the existence of rotational isomers will remain until further experimental evidence is offered.

In the present paper, from the investigation of the Raman and infrared spectra and measurements of the dipole moments of the two compounds, in addition to identifying the cis and trans compounds, we will show that the cis compound* having the higher boiling point consists of a single molecular species which has a non-planar configuration and that the trans compound* having the lower boiling point consists of two rotational isomers, both of which have planar configurations.

## Experimental

**Preparation of the Samples.**—Both *cis*- and *trans*-$\beta$-chlorovinyl methyl ethers were prepared by workers in this laboratory. The samples were purified by fractional distillation. The boiling points of the cis and trans compounds were 105~106°C and 85~86°C respectively. Although a small amount of the cis compound had not been perfectly removed from the trans compound, it did not disturb the interpretation of the spectra to a large extent.

**Infrared Absorption Spectra.**—Infrared spectra were obtained by a Perkin-Elmer model 21 spectrometer equipped with sodium chloride, calcium fluoride and potassium bromide prisms. Vapor spectra were recorded at 130~150°C using a heated 5 cm. cell[4]. For the trans compound, the spectra in the solid state were also measured, using a low temperature cell[4] constructed in our laboratory. The spectra are reproduced in Figs. 2 and 3, and the data are tabulated in Tables I and II. Since the solvent effect was not found in any appreciable amount, the spectra in solutions are not reproduced here.

**Raman Spectra.**—Raman spectra were obtained using 4358 Å excitation with a three-prism spectrograph (17 Å/mm. at 4358 Å) constructed in this laboratory. A low-pressure mercury arc lamp was used. A double layer composed of a sodium nitrate solution (40 g./100 g. solution) and a Rhodamine 6G dilute solution was used as a liquid filter. Exposure was for from one to six hours. The data are tabulated in the first columns of Tables I and II. Approximate line intensities on the photographic plates are indicated by the numbers in parentheses.

**Dipole Moments.**—The dielectric constants of the benzene solution of the compounds were observed in several dilutions at 20~60°C. Densities were also measured by a pycnometer. From those values, the dipole moments were calculated by the conventional way; 2.53 D was obtained for the cis compound, and 1.6 D for the trans compound, at 25°C. It was also found that, as to the trans compound, its dipole moment did not depend on the temperature in the range 20~60°C.

## Discussion

**Rotational Isomers.**—As can be seen in Figs. 2b and 3b, the spectrum of the trans compound in the liquid state is very complicated compared with that of the cis compound. Thirteen absorption bands are theoretically expected in the 600~1700 $cm^{-1}$ region for this compound. Nevertheless, nineteen bands are observed for the trans compound in liquid. Since most of the bands have fairly strong intensities and their intensities did not change through repeated purifications of the samples, those bands are believed to be inherent to the molecule and not to come from impurities. Furthermore, the fact that some bands disappeared on the solidification of the sample (see Fig. 3c), is strong evidence for the presence of rotational isomers in the liquid. The number of bands in the solid spectra is in accordance with the theoretical expectations. That means the trans compound in the liquid state is a mixture of two or more rotational isomers, and that, in the course of solidification, every molecule takes on an unique configuration suitable for the low temperature by rotating the methoxy group around the C–O bond axis. On the other hand, the liquid spectrum of the cis compound is very simple, and the numbers of bands is so few that it seems possible that only one molecular species seems to exist.

**Dipole Moments.**—The dipole moments are estimated for both the trans and cis compounds on the basis of the vector model shown in

1) Y. Mikawa, This Bulletin, **29**, 110 (1956).
2) W. H. T. Davison and G. R. Bates, *J. Chem. Soc.*, **1953**, 2607.
3) A. Kirrman and P. Chancel, *Bull. soc. chim. France* **1954**, 1338.
* In the following sections, for convenience, the terms "the cis and trans compounds" will be used for denoting the compounds having the higher and lower boiling points respectively.
4) S. Mizushima, "Structure of Molecules and Internal Rotation", Acad. Press, New York (1954).

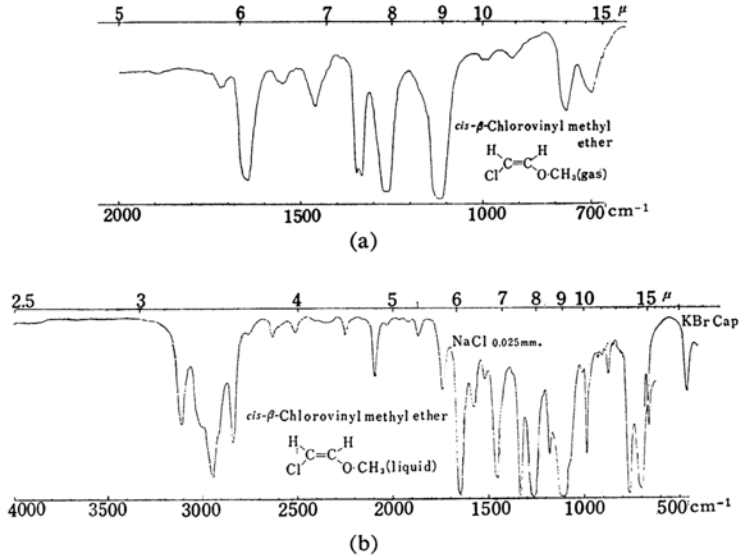



Fig. 2. Infrared absorption spectra of *cis*-chlorovinyl methyl ether. (a) Vapor at ca. 130°C; (b) Liquid film at the room temperature.

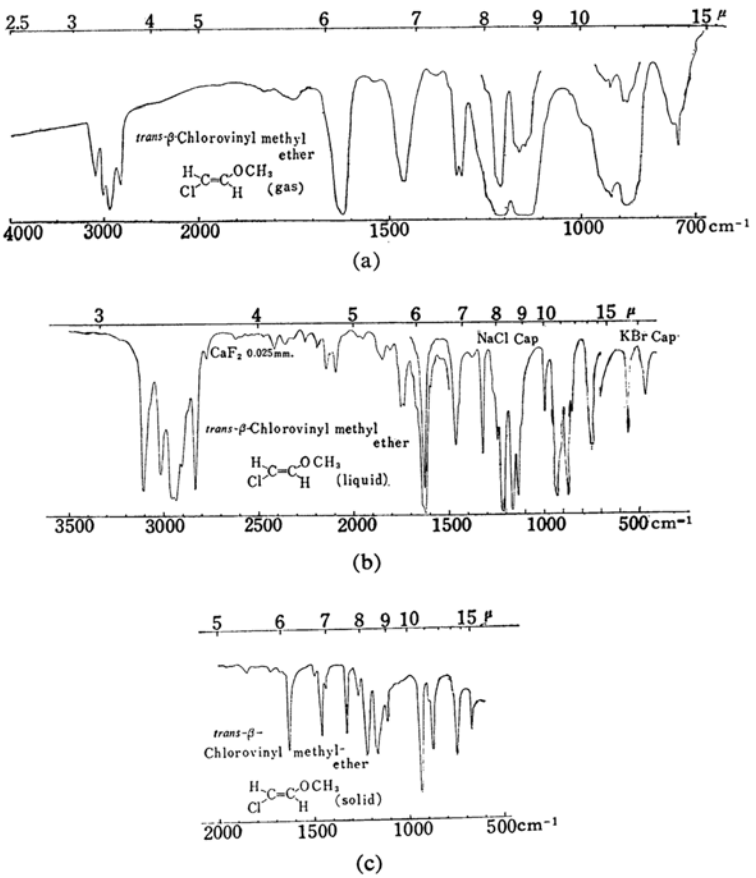



Fig. 3. Infrared absorption spectra of *trans*-chlorovinyl methyl ether. (a) Vapor at ca. 130°C; (b) Liquid film at the room temperature; (c) Solid at ca. −190°C.

TABLE I. THE VIBRATIONAL SPECTRA OF *cis*-β-CHLOROVINYL METHYL ETHER

| Raman data Liquid | Infrared data Vapor | Infrared data Liquid | Assignment |
|---|---|---|---|
| 173 ( 5) | | | |
| 359 ( 4) | | | |
| 466 ( 6) | | 460m | Skeletal vibration |
| 667 ( 5) | | 662w | |
| 707 ( 0) | 700w | 703vs | =CH out-of-plane bend. |
| 763 ( 7) | 768w | 763vs | C–Cl stretch. |
| 879 ( 5) | | 873w | =CH out-of-plane bend. |
| 918 ( 0) | 918w | 908vw | |
| | 985, 988 w | 998m | C–O–C sym. stretch. |
| | | 1010w | |
| | | 1050sh | |
| 1080 ( 2) | | 1070sh | $CH_3$ wag. |
| | 1118vs | 1110vs | C–O–C anti-sym. stretch. |
| 1185 ( 4) | 1175sh | 1181m | $CH_3$ rock. |
| 1265 ( 6) | 1260, 1268 vs | 1261vs | =CH in-plane bend. |
| 1337 ( 4) | 1333, 1345 m | 1331 s | =CH in-plane bend. |
| | | 1430sh | $CH_3$ asym. deformation |
| 1463 ( 5) | 1459w | 1452 s | $CH_3$ sym. deformation |
| | | 1520vw | |
| | 1552w | | |
| | | 1578vw | |
| 1655 (10) | 1647, 1665 m | 1650 s | C=C stretch. |
| | 1713, 1720 w | 1740w | |
| | | 1870vw | |
| | | 2098w | |
| | | 2250w | |
| | | 2510vw | |
| | | 2630vw | |
| 2842 ( 6) | | 2842m | $CH_3$ sym. stretch. |
| 2950 ( 9) | | 2947 s | $CH_3$ asym. stretch. |
| 3050 | | 3000sh | CH sym. stretch. |
| 3100 | | 3112m | CH asym. stretch. |

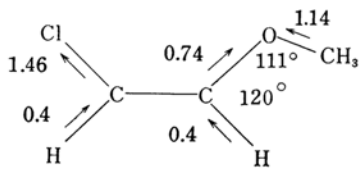



Fig. 4. Bond moments of chlorovinyl methyl ether.

Fig. 4*. It should be noted that the estimated values for the trans compound did not depend upon the angle of internal rotation. The estimated value, 1.55 D, is in good agreement with the observed value, 1.6 D. The fact that the observed values remained constant within the temperature range of 20~60°C does not contradict the presumption of rotational isomers, because even if the ratio of the number of the two rotational isomers varies with the temperature of the system, the dipole moment of the whole system should not change.

As for the cis compound, the estimated dipole moments are 3.08, 2.55 and 1.75 D as the angle of rotation, $\tau$, increases from 0° to 90° and 180° (corresponding to the zigzag, the non-planar and the bent form respectively). Since the observed value was 2.53, the results of the calculation indicate that, as far as the bond moments approximation is valid, the molecule in the solution at 25°C takes on a non-planar configuration with an angle of internal rotation of about 90°.

At any rate, there is no doubt that the "trans compound" having a lower boiling point has a trans configuration and that the "cis compound" has a cis configuration.

* In Fig. 4. the figure for the cis molecule is given. The same bond moments are used for the trans molecule.

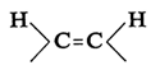
TABLE II. THE VIBRATIONAL SPECTRA OF *trans*-β-CHLOROVINYL METHYL ETHER

| Raman data Liquid | Infrared data Vapor | Infrared data Liquid | Infrared data Solid | Assignment |
|---|---|---|---|---|
| 142 (4) | | | | Skeletal vibration |
| 220 (0) | | | | |
| 327 (6) | | | | |
| 415 (3) | | | | |
| 457 (0) | | | | |
| 553 (2) | | | | |
| | | | 668w | Impurity |
| 742 (4) | 746m | 745m | 746 s | C-Cl stretch. |
| 757 (2) | 760sh | 765sh | | L. |
| | 855sh, 866sh | 850m | | L. |
| | 879m, 890m | 872 s | 874m | =CH out-of-plane bend. |
| | | 910sh | | |
| 932 (5) | 924m | 928 s | 932 s | C-O-C sym. stretch. |
| | 935sh | 940sh | | |
| 987 (2) | 985sh | 992m | | L. |
| | | 1110sh | 1111m | |
| | 1135sh, 1146 s | 1133 s | | L. |
| 1161 (1) | 1162 s, 1170sh | 1160 s | 1162 s | =CH in-plane bend. |
| 1210 (2) | 1212vs | 1210 s | 1214 s | C-O-C anti-sym. stretch. |
| 1248 (5) | 1250sh | 1240m | | |
| | | 1260sh | 1261m | $CH_3$ rock. |
| 1316 (7) | 1314m, 1325m | 1320 s | 1322 s | =CH in-plane bend. |
| | 1377w | 1370w | | |
| 1445 (4) | | 1445sh | 1436w | $CH_3$ asym. deformation |
| 1450 (4b) | 1462 s | 1460 s | 1454 s | $CH_3$ sym. deformation |
| | | | 1490w | |
| 1623 (9) | 1623 s | 1623 s | 1630 s | C=C stretch. |
| 1637 (6) | 1635sh | 1640sh | | L. |
| | | 1732w | | |
| | | 1750w | | |
| | | 1806vw | | |
| | | 1845w | | |
| | | 1950vw | | |
| | | 1973vw | | |
| | | 2090w | | |
| | | 2116vw | | |
| | | 2140w | | |
| | | 2190vw | | |
| | | 2251vw | | |
| | | 2310vw | | |
| | | 2360vw | | |
| | | 2416vw | | |
| | | 2772vw | | |
| 2830 (6) | 2835 s | 2832 s | | $CH_3$ sym. stretch. |
| | | 2902sh | | |
| 2946 (9) | 2945 s | 2934, 2956 s | | $CH_3$ asym. stretch. |
| 3012 (5) | 3005 s | 3010 s | | CH sym. stretch. |
| 3100 (4) | 3090 s | 3103 s | | CH asym. stretch. |

s=strong, m=medium, w=weak, vw=very weak, sh=shoulder
L=Bands arising from the less stable form of the molecule

**Vibrational Spectra.**—*cis-Chlorovinyl Methyl Ether.*—It can be seen from Table I that most of the Raman bands are also observed in the infrared spectra and that, except for the rotational structure of the vapor spectra, no essential difference between the infrared absorption frequencies measured in the liquid and vapor states is found. Furthermore, the number of the absorption bands is in accordance with the expectations. These facts exclude the possibility of the existence of the rotational isomers in the liquid or the vapor state. This exhibits a contrast to the trans compound, which will be mentioned later.

The observed frequencies can be interpreted as a superposition of the characteristic frequencies of vinyl and ether compounds. For instance, the bands at 1655, 1337, 1265 and 879 $cm^{-1}$ correspond to those at 1601, 1360, 1271 and 908 $cm^{-1}$ [5] of vinyl chloride. The fact that C=C stretching and =CH out-of-plane frequencies appear at 1655 and 707 $cm^{-1}$ respectively gives strong spectroscopic evidence for the cis configuration, because the compound having the group



has, in general, two distinct characteristic bands in the regions 1635~1675 and 665~730 $cm^{-1}$ [6]. The bands, at 466, 988 and 1118 $cm^{-1}$ are due to the ether linkage, corresponding to those of dimethyl ether at 418, 929 and 1115 $cm^{-1}$, which were assigned[7] to the COC bending, symmetric and anti-symmetric stretching vibration respectively.

As was discussed in the previous study[1], methyl vinyl ether and other alkyl vinyl ethers have characteristic frequencies which distinctly differ from compounds having a vinyl group alone or an ether group alone, and the spectra of vinyl ethers can be interpreted on the assumption of a planar configuration. The reason why the cis compound concerned does not have the characteristic frequencies of vinyl ether can be explained only by rejecting the assumption of a planar configuration, i. e., by assming instead that the molecule of the cis compound takes on a non-planar configuration. In this case no resonance effect is taken into consideration, and consequently, the force constant of –C=C– or –C–O– keeps its original value. Therefore, some of the bands characteristic of vinyl compounds and ethers can be expected in the cis compound.

Though the angle of internal rotation cannot be predicted from the spectroscopic data, the conclusion is in conformity with that deduced from dipole moment measurement.

*trans-Chlorovinyl Methyl Ether.*—Several bands of the liquid spectra disappeared in the solid spectra. The bands which remain in the solid spectra are considered to be the spectra arising from the stable form of the rotational isomers. From this point of view, the liquid spectra as well as the vapor spectra were interpreted as superposed spectra of two or more configurational isomers, and the bands belonging to the stable form were tentatively assigned on the basis of an assumed model.

In the vapor spectrum (see Fig 3a), the band at 1322 $cm^{-1}$ shows a very distinctive band shape. As will be seen later, this band is assigned to the =CH in-plane bending mode. The C=C stretching mode is expected around 1650 $cm^{-1}$, and it is known that the frequency of the trans compound usually appears at a higher frequency range than of the corresponding cis compound. However, in the present case, a strong band to be assigned to C=C stretching mode appears at 1623 $cm^{-1}$, or on the lower frequency side of the corresponding band of the cis compound. Furthermore, the general features of the spectra of this compound have a strong resemblance to those of methyl vinyl ether. The correlation between the two compounds is given in Table III. Based on these considerations, the molecular configuration of the stable form of the trans compound is supposed to be planar in form, probably the zigzag form, which had been shown to be plausible in the case of methyl vinyl ether. Thus, the assignment for most of bands was performed by reference to methyl vinyl ether. Though conclusive assignments are not possible at this stage, tentative assignment are shown in Table II.

TABLE III. CORRELATION BETWEEN THE BANDS OF *trans*-CHLOROVINYL METHYL ETHER AND THOSE OF VINYL METHYL ETHER

| Vinyl methyl ether $cm^{-1}$ | *trans*-Chlorovinyl methyl ether, $cm^{-1}$ |
|---|---|
| 1618 | 1623 |
| 1325 | 1320 |
| 1225 | 1212 |
| 1140 | 1166 |
| 965 | 924 |
| 886 | 885 |

In the liquid and vapor spectra, there exist several bands which vanish in the solid state. These bands presumably belong to another rotational isomer existing in the liquid or vapor. Though the configuration of the

5) Landolt-Börnstein, "Zahlenwerte und Funktionen" 6, Anflage, I. Band, 2. Teil, Springer-Verlag, (1951).
6) A. D. Cross, "An Introduction to Practical Infrared Spectroscopy", Butterworth, London (1960).
7) Y. Mashiko, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 470 (1958).

TABLE IV. MOMENTS OF INERTIA OF *trans*-CHLOROVINYL METHYL ETHER AND THEIR DIRECTION COSINES

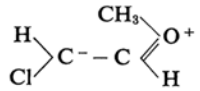
$\tau=0$ (Zigzag form)

| | $I_A$ | $I_B$ | $I_C$ |
|---|---|---|---|
| Moment of inertia ($\times10^{-40}$ g. cm$^2$) | 601.2 | 573.0 | 33.28 |
| Direction cosine $l$ | 0 | 0.545 | 0.838 |
| $m$ | 0 | −0.838 | 0.545 |
| $n$ | 1 | 0 | 0 |

$\tau=180°$ (Bent form)

| | $I_A$ | $I_B$ | $I_C$ |
|---|---|---|---|
| Moment of inertia ($\times10^{-40}$ g. cm$^2$) | 516.7 | 469.1 | 52.74 |
| Direction cosine $l$ | 0 | 0.608 | 0.794 |
| $m$ | 0 | −0.794 | 0.608 |
| $n$ | 1 | 0 | 0 |

unstable form cannot be decided on, it may be supposed to be a planar-bent form which is stabilized by the contribution of the resonance structure

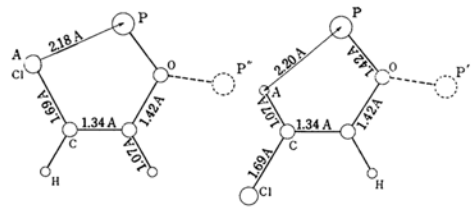


for the C=C frequency at 1635 cm$^{-1}$ is still lower than that of the cis compound.

*The Band Shape.*—The moments of inertia and the direction cosines of the three principal axes of the trans molecule (in the zigzag form) are listed in Table IV. The bond lengths and the bond angles adopted in the calculation are shown in Fig. 5b. The calculation was carried out for every 30° from 0 to 180° of $\tau$, and it was found that the symmetric top model could be approximately applied in every case. The degree of separation between the P and R branches of the parallel bands was estimated by the Gerhard-Dennison method[8], being found within the values 11.25 and 12.17 cm$^{-1}$ at 400°K for any value of $\tau$. The observed separation, 12 cm$^{-1}$, at the 1322 cm$^{-1}$ band is in good agreement with the predicted value.

The exact modes of the normal vibrations can be pictured only by the normal coordinate treatment of the molecule. However, if the C–H in-plane bending vibration is localized in C–H bonds and there is on mixing with the other mode, the direction of the change of dipole moment can be decided upon. Therefore, it is easy to calculate the angle between one of the principal axes of the moment of inertia and the direction of the change of the bond moment of the C–H in-plane vibration. The calculated values for the zigzag and the bent forms of the trans compounds were 3°30′ and 7° respectively; i. e. the bands, in both cases, should exhibit an almost pure parallel type. Thus, for the C–H in-plane vibration, it is predicted that the band shape and the frequency do not change appreciably no matter what value the angle of internal rotation takes. This is why the band at 1322 cm$^{-1}$ is assigned to the C–H in plane mode.

Many bands beside 1322 cm$^{-1}$ show very complex band shapes. The band features of these bands are interpreted as the overlapping of two bands. For instance, the band at 1130～1170 cm$^{-1}$ is composed of two doublets; the one is of 1135 cm$^{-1}$ and 1146 cm$^{-1}$, and the other is of 1162 cm$^{-1}$ and 1170 cm$^{-1}$. Similarly, the band at 850～890 cm$^{-1}$ is composed of the doublets of 855 cm$^{-1}$ and 865 cm$^{-1}$, and of 881 cm$^{-1}$ and 891 cm$^{-1}$. These doublets are separated by 8～11 cm$^{-1}$, a separation compatible with the calculated value within the margins of experimental error.




(a) *cis*-Chlorovinyl methyl ether (b) *trans*-Chlorovinyl methyl ether

Fig. 5. The molecular configurations of chlorovinyl methyl ethers.

**Internal Potential.**—In the preceding sections, it was concluded that the cis compound takes just one non-planar configuration, while the trans compound in the liquid or vapor states two types of configuration, both of which are considered to be planar. It is of interest to discuss the internal forces which determine the stable configuration of the rotational isomers.

Three main factors are taken into consideration:

8) S. L. Gerhard and D. M. Dennison, *Phys. Rev.*, **43**, 197 (1933).

TABLE V. DIPOLE INTERACTION ENERGY (kcal./mol.)

| Angle of internal rotation | Cis-compound | | | Trans-compound |
|---|---|---|---|---|
| | $\rho=0.4$ | $\rho=0.5$ | $\rho=0.7$ | $\rho=0.5$ |
| 0° (zigzag) | 0.55 | 0.96 | 1.30 | 1.17 |
| 90° (non-planar) | 0.14 | 0.37 | 0.28 | 0.92 |
| 180° (bent) | −1.49 | −1.28 | −1.13 | 1.17 |

i) The steric repulsion
ii) The contribution of the resonance structure, $C^--C=O^+$
iii) The electrostatic force

First, the steric repulsion of the non-bonded atom in the molecule must be considered. Interatomic distances are shown in Fig. 5. If the methyl group is situated at P (Fig. 5), the interaction between the group at P and the atom at A becomes prominent. Especially for the cis compound, the distance between A and P is 2.18 Å, much less than the sum of the van der Waals radii of the chlorine atom and the methyl group. Consequently, the methyl group cannot be situated at P on the plane of the vinyl group. Thus, the bent form is excluded from consideration for the cis compounds. Secondly, the resonance effect has to be considered. From the infrared study[1], it was concluded that in vinyl ether there was an appreciable single bond-double bond resonance. Therefore, the resonance effect would be of considerable importance for the chlorovinyl ethers concerned. If there is no other predominant factor than the resonance effect, the planar configurations, both the bent and the zigzag forms, become the stable forms. Such is the case with the trans compound. As has deen described before, the infrared spectra and the observed dipole moment are compatible with this model. However, as to the cis compound, the other effect seems to dominate over the resonance effect. The electrostatic interaction plays a significant role in this case, as will be shown below.

The interaction energy between two dipoles, $\mu_1$ and $\mu_2$, can be evaluated by the equation:

$$\mu_1\mu_2(\cos\theta-3\cos\alpha\cdot\cos\beta)/R \qquad (4)$$

where $R$ is the distance between the dipoles, $\theta$ denotes the angle betwee $\mu_1$ and $\mu_2$, and $\alpha$ or $\beta$ denotes the angle between one of the dipoles and the line connecting the two. On the base of the bond moments as shown in Fig. 4, the interaction energy of the dipoles was calculated with several values of $\tau$, varying from 0 to 180°. Some of the results are listed in Table V, where the $\rho$ value, which is a parameter which decides the apparent position of a dipole on the line connecting the atoms cencerned, is assumed to be 0.4, 0.5, or 0.7 for the cis compound. From Table V it can be seen that the difference between the values at $\tau=0°$ and $\tau=180°$ does not seriously depend upon the choice of the $\rho$ value. In the cis compound, the bent form is more stable by 2.2±0.2 kcal, than the zigzag form. As to the trans compound, the dipole-dipole interaction seems to be minor; the zigzag, the non-planar and the bent forms have almost the same energy in so far as the electrostatic forces are concerned.

Form the consideration of these three factors, it is concluded that the trans compound takes the zigzag form as the most stable configuration, and that if the resonance energy overcomes the steric repulsion, the bent form also becomes stable. The non-planar configuration is unfavorable in all respects. On the other hand, as to the cis compound, the zigzag form is not always the most stable because it can have a higher energy than the non-planar form; i. e., if the amount of resonance energy is quite small in comparison with the dipole-dipole interaction, the zigzag form is less stable than the non-planar form. Although many other factors beside the three mentioned above could be considered in connection with the internal rotation, and although the estimation of the dipole-dipole interaction was made only roughly, it is sure that the dipole-dipole interaction plays a significant role in the cis compound which takes the non-planar configuration.

## Summary

Raman and infrared spectra of *cis*- and *trans*-β-chlorovinyl methyl ethers ($ClCHCHOCH_3$) were measured in the vapor and liquid states, and the infrared spectra in the solid state were also measured for the trans compound. The dipole moments were measured for both of the compounds in a benzene solution. From the observed value of the dipole moments, it was decided that the compound having the lower boiling point had a trans configuration and the other, a cis configuration.

On the basis of these configuration, interpretation of the vibrational spectra of both compounds was undertaken. As for the trans compound, the existence of the rotational isomers arising from the internal rotation around the C–O axis was verified by the fact that some of the infrared bands disappeared on solidification of the samples. The spectra

in the liquid and vapor states were interpreted as a mixture of those of two rotational isomers, and tentative assignments were given for one of the isomers by reference to the spectra of methyl vinyl ether. The most probable form of the molecule was supposed as the planar zigzag form.

On the contrary, it was established that there existed no rotational isomer in the cis compound in any state. The spectra of the cis compound did not resemble those of the trans compound or the methyl vinyl ether and were interpreted as a superposition of group frequencies of the ether linkage and of the -CH=CH- group. Consequently, a non-planar model was proposed, and the angle of internal rotation was determined to be about 90° from the observed value of the dipole moment. In order to explain the difference in the spacial configuration between the cis and the trans compounds, the electrostatic effect, in addition to the resonance effect and the steric repulsion, was considered. From the results of the calculation of the dipole-dipole interaction, it was shown that this electrostatic force played a very significant role in the internal rotation.

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