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The Molecular Structure of Vinylidene Chloride by Different Methods of Electron Diffraction[1,2]

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The molecular structure of vinylidene chloride has been studied by the visual method using non-sectored and sectored plates and by the sector-microphotometer method. The results of the different methods are compared and discussed. The structural parameters have been found to be: C–C = 1.324 ± 0.020 Å., C–Cl = 1.710 ± 0.010 Å. and ∠ClCCl = 114.5 ± 1°.

Early electron diffraction work on the structures of the chloroethenes[4] suggested that there was an increase in the C–Cl distances in these compounds as the number of chlorine atoms adjacent to the double bond was increased. This increase was attributed[5] to the decrease in the degree of double bond character possessed by the C–Cl bonds with the addition of each chlorine atom. Although the early work suggested the trend in the C–Cl distances, the uncertainties attached to the determinations were rather large. This is not surprising since the experimental diffraction patterns extended to a maximum q value of about 50 in the case of vinylidene chloride (1,1-dichloroethene). These considerations, as well as the advances which have been made in electron diffraction techniques, suggested that a reinvestigation might yield more accurate molecular parameters for these compounds. Further, it was our intention to compare some of the different methods of electron diffraction. For this purpose vinylidene chloride was chosen as the experimental molecule.

Experimental

Vinylidene chloride, obtained from the Matheson Company, was distilled under vacuum several times and the purity of the sample was found to be better than 99% by a cooling curve analysis. The optimum vapor pressure for the purpose of taking diffraction patterns was found to be about 30 mm. The apparatus used for taking the diffraction photographs has been described by Kristoff.[6]

A series of photographs was obtained using Kodak Lantern Slide Medium plates and electrons of wave length 0.05452 Å., for the purpose of a visual investigation of the structure. No rotating sector was employed in taking this series of photographs. Five patterns were used for measurements, two taken from a camera distance of 25.015 cm. and three taken from a camera distance of 10.192 cm. The visual curve is based on measurements of the features and intensity estimates by two independent observers. The curve extends to a q value of about 113 and is shown in Fig. 1. (The variable q is equal to $40/\lambda \sin \theta/2$ where θ is the angle of scattering and λ is the electron wave length.)

Several sets of photographs of the compound were taken at both the long and short camera distances with Kodak Lantern Slide Contrast plates using an r^3 sector and electrons of wave length 0.05452 Å.

A visual intensity curve was obtained from these sectored plates making use of two patterns taken at the long camera distance and four at the short camera distance. These sector-visual data extend from a q value of about 16 to a q value of about 120 as shown in Fig. 1.

Microphotometer traces were taken on a Leeds and Northrup microphotometer for two plates at each camera distance, while rotating the plates at high speed.[7] The transmittances obtained from the traces were converted to intensities by the method described by Karle and Karle,[8] averaged and plotted against q. The total range of usable data extends from $q = 14$ to $q = 100$. The molecular scattering intensities were obtained from the total intensity data by means of the equation

$$I_m(q) = qK\left[\frac{I_t(q)}{I_b(q)} - 1\right] \tag{1}$$

where $I_m(q)$ is the molecular scattering function to be compared with calculated intensity curves, $I_t(q)$ is the total intensity, $I_b(q)$ is the background intensity (which must be estimated) and K is a constant.

The radial distribution procedure was employed by calculation of curves using the equation[9]

$$rD(r) = \sum_{q=1,2,3\ldots}^{q_{\max}} I_m(q) \exp(-bq^2) \sin \frac{\pi q r}{10} \tag{2}$$

where $rD(r)$ is the radial distribution function, r is the internuclear separation and $\exp(-bq^2) = 0.10$ for $q = q_{\max}$.

One radial distribution curve was calculated from the visual intensity curve from non-sectored plates and one was calculated from the visual curve from sectored plates; these curves are shown in Fig. 3. For both curves data for the range $q = 0$ to $q = 15$ were obtained from a theoretical intensity curve, calculated by the formula[9]

$$I_m(q) = \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}} \exp(-b_{ij} q^2) \sin \frac{\pi q r_{ij}}{10} \tag{3}$$

by means of punched cards. (Z represents atomic number and r_{ij} is the separation of the ith and jth nuclei.)

The final radial distribution curve from the sector-microphotometer data was obtained in the following way: using intensity data obtained from the microphotometer traces and the first background line, a preliminary radial distribution curve was calculated. The parameters obtained from the major peaks of this curve were then used to calculate a theoretical intensity curve by equation 3. The inner portion of this curve ($q = 0$ to $q = 13$) was then added to the experimental intensity curve and a second radial distribution curve calculated. Several additional curves were calculated by making successive improvements in the background line; by this procedure each curve showed smaller negative areas than the previous one. The final molecular intensity curve is shown in Fig. 1 and the final radial distribution curve in Fig. 4.

Results and Discussion

The radial distribution curve from the visual data shows major peaks at 1.34, 1.71 and 2.87 Å. corresponding to the C–C, C–Cl and Cl· · ·Cl distances, respectively. The Cl· · ·Cl peak at 2.87 Å. has a shoulder which probably is due to a combina-

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(1) Contains material from the Ph.D. theses of C. N. R. Rao and L. H. Kaplan and the M.S. thesis of L. Rocks.

(2) Presented before the Division of Physical Chemistry at the 133rd Meeting, American Chemical Society, San Francisco, California, April, 1958.

(3) Purdue Research Foundation Fellow in Chemistry, 1956–1957; Standard Oil Foundation Fellow in Chemistry, 1957–1958.

(4) L. O. Brockway, J. Y. Beach and L. Pauling, THIS JOURNAL, **57**, 2693 (1935).

(5) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

(6) J. J. Kristoff, Jr., Ph.D. Thesis, Purdue University, 1958.

(7) I. L. Karle, D. Hoober and J. Karle, *J. Chem. Phys.*, **15**, 765 (1947).

(8) J. Karle and I. L. Karle, *ibid.*, **17**, 1052 (1949).

(9) P. A. Shaffer, Jr., V. Schomaker and L. Pauling, *ibid.*, **14**, 659 (1946).

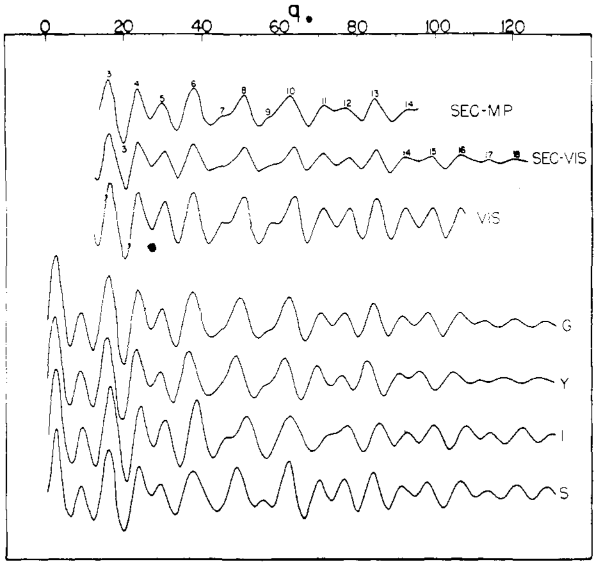

Fig. 1.—Experimental and theoretical intensity curves for vinylidene chloride.

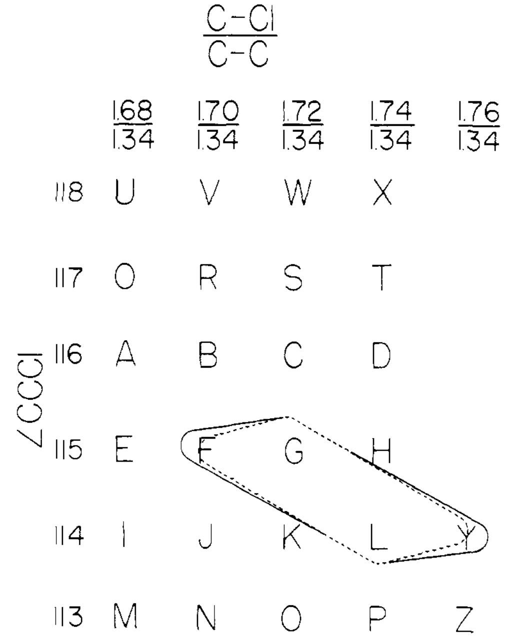

Fig. 2.—Parameter chart for vinylidene chloride. The solid line represents the acceptable parameter field by the visual method using non-sectored plates; the dotted line represents the acceptable parameter field by the sector-visual and the sector-microphotometer methods.

tion of C· · ·Cl and H· · ·Cl (short) distances. The peak observed at 0.93 Å. probably is due to the C–H distance. Peaks corresponding to the C· · ·H and H· · ·Cl (long) distances are not reliable, since there are extraneous features in these regions with comparable amplitudes.

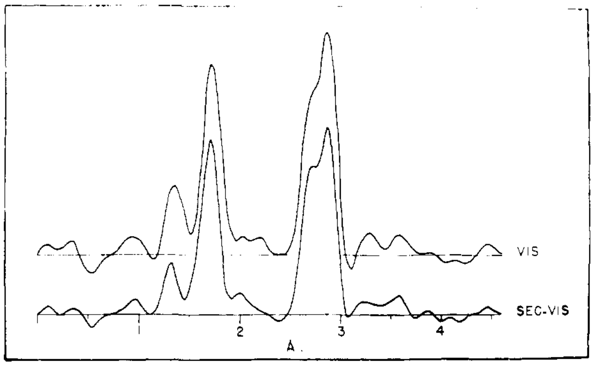

Fig. 3.—Radial distribution curves for vinylidene chloride from the visual and the sector-visual data.

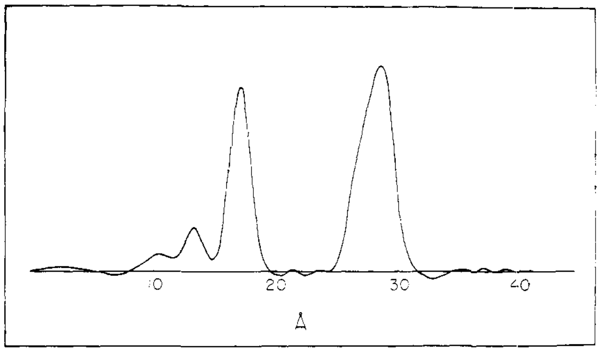

Fig. 4.—Radial distribution curve for vinylidene chloride from the sector-microphotometer data.

The radial distribution curve from the sector-visual data shows major peaks at 1.32_2, 1.70_8 and 2.86_6 Å. The peak at 2.86_6 Å. shows a prominent shoulder around 2.72 Å. which should represent a combination of the C· · ·Cl and H· · ·Cl (short) distances. The peaks corresponding to the C–C, C–Cl and Cl—Cl distances could be fitted reasonably well by the Karles' method[8,10,11] using h_{ij} values of 312, 200 and 111 respectively, which are in good agreement with the values proposed by Morino, *et al.*[12] There are three small peaks at 0.96_4, 2.00_4 and 3.59_0 Å. corresponding to the C–H, C· · ·H and H· · ·Cl (long) distances, respectively. The areas of the different peaks are in good agreement with the calculated nZ_iZ_j/r values. The results of the radial distribution curve by the sector-visual method are compared with the results of the radial distribution curve by the sector-microphotometer method in Table I.

TABLE I

RESULTS OF THE RADIAL DISTRIBUTION CURVES BY THE SECTOR-MICROPHOTOMETER AND SECTOR-VISUAL METHODS

	Sector-microphotometer method			Sector-visual method		
Distance	r_{ij}, Å.	h_{ij}	Area	r_{ij}, Å.	Area	$\frac{nZ_iZ_j}{r_{ij}}$[a]
C–H	1.040	100	9.5	0.96_4	8.3	11.8
C–C	1.324	300	23.4	1.32_2	24.0	22.8
C–Cl	1.710	200	100.0	1.70_8	100.0	100.0
C· · ·Cl	2.665	180	57.8	. . .	. . .	63.9
Cl· · ·Cl	2.864	110	97.3	2.86_6	98.9	84.3

[a] These values have been multiplied by a factor chosen to make the value for the C–Cl distance equal to 100.

The final radial distribution curve (Fig. 4) calculated by the sector-microphotometer method showed major peaks at 1.710 Å. and 2.864 Å. representing the C–Cl distance and a combination of

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(10) J. Karle and I. L. Karle, *J. Chem. Phys.*, **18**, 957 (1950).

(11) I. L. Karle and J. Karle, *ibid.*, **18**, 963 (1950).

(12) Morino, Kuchitsu, Takahashi and Maeda, *ibid.*, **21**, 1927 (1953).

C···Cl, Cl···Cl and H···Cl distances, respectively. It also shows smaller peaks at 1.040 Å. and 1.324 Å., representing the C–H and C–C distances, respectively. The composite peak at 2.864 Å. was resolved according to the method described by Karle and Karle[10] and was found to be consistent with the distances C···Cl = 2.664 Å., Cl···Cl = 2.864 Å. and H···Cl = 2.85 Å. The ∠ CCCl calculated on the basis of these distances was found to be 122.8 ± 0.5°. The root mean square amplitudes of vibration of the different atom pairs and the areas of the peaks are given in Table I.

Although the radial distribution curve calculated from the visual intensity curve from non-sectored plates gives the major distances (the C–Cl and Cl···Cl) rather correctly, it is less reliable because of the large negative areas and extraneous features. The C–C distance, which has a relatively smaller contribution to scattering, is not obtained correctly. While the sector-visual radial distribution curve shows a few small negative regions and some so-called diffraction effects, it is definitely more reliable, as demonstrated by the areas of the peaks and fitting of at least some of the peaks by the Karles' method. It has been found that the effect of the uncertainties in the visual intensity estimates (from sectored plates) of the sensitive features on the interatomic distances is almost negligible for this compound. The results of additional calculations indicate that the intensity data up to a q value of 90 provide sufficient information to establish the structure of vinylidene chloride, although better resolution of the radial distribution peaks is obtained when more data are used.

In order to carry out the correlation procedure, several theoretical intensity curves were calculated using equation 3, assuming constant coefficients, a C–H distance of 1.07 Å. and a CCH angle of 120°. The root mean square amplitudes of vibrations used for the different atom pairs were taken from the results of the radial distribution curve (Table I) and from Morino, *et al.*,[12] and Coutts and Livingston.[13] The extent of the parameter field chosen for investigation is shown in Fig. 2. A few selected theoretical intensity curves are shown in Fig. 1. In addition to these models, Model G was calculated with variable coefficients[14] taking into account the atomic X-ray scattering factors[15] and the peak locations in the latter curve agreed almost exactly with the curve calculated assuming constant coefficients. Although there were large differences in intensities at very low q values, the curves for models calculated with constant coefficients are sufficiently good approximations within the range of experimental data used.

The correlation procedure was first carried out with the visual intensity curve from non-sectored plates. Certain models were rejected on the basis of their qualitative disagreement. Models B, C, D, H, K and S fail to reproduce the observed curve in that they give rise to curves which show no seventh maximum. These curves are illustrated by curve S in Fig. 1 which is typical of the group. Model D also lacks a sufficiently strong maximum 11. Models A, E, I, J, P and Z do not show a sufficiently well defined ninth maximum, as typified by curve I in Fig. 1. Further, curves A, E, I and J also lack a sufficiently strong maximum 11. Qualitatively, models F, G, L and Y are acceptable and they show mean $q_{\text{calc}}/q_{\text{obs}}$ values of 1.000, 0.992, 0.983 and 0.976 with average deviations from the mean of 0.008, 0.006, 0.006 and 0.009, respectively. Minima 7 and 9 were omitted as being unreliable for the quantitative correlation. The parameters of vinylidene chloride obtained from this correlation are as follows: ∠ ClCCl = 114.5 ± 1°, C–C = 1.32 ± 0.03 Å. and C–Cl = 1.71 ± 0.02 Å.

The correlation procedure with the visual intensity curve from sectored plates indicated that the models G and L are acceptable and that F and Y have to be considered as borderline cases; model Y does not show maximum 7 clearly while model F shows maximum 12 higher than maximum 11. For purposes of quantitative correlation, maximum 7, minimum 7, minimum 9 and maximum 9 were omitted as unreliable. Models F, G, L and Y gave mean $q_{\text{calcd}}/q_{\text{obsd}}$ ratios of 1.000, 0.991, 0.983 and 0.976, and average deviations of 0.008, 0.005, 0.005 and 0.007, respectively. Placing double weight on models G and L, the parameters are calculated to be: ∠ ClCCl = 114.5 ± 1°, C–C = $1.32 \pm 0.02_5$ Å., C–Cl = $1.71 \pm 0.01_5$ Å.

The results of the correlation procedure with the sector-microphotometer intensity curve were similar to the results of the sector-visual intensity curve. The observed q values by the sector-microphotometer method and the quantitative electron diffraction data for models F, G, L and Y are given in Table II. For purposes of comparison, the quantitative data for model G by the visual and the sector-visual methods also are included. The principal parameters calculated for the models F, G, L and Y are given in Table III.

The radial distribution values are taken as the final results with uncertainties established by the correlation procedure: C–C = 1.324 ± 0.020 Å., C–Cl = 1.710 ± 0.010 Å. and ∠ClCCl = 114.5 ± 1°.

The results of the visual correlation procedure with the intensity curves from sectored and non-sectored plates show excellent agreement with each other and also with the results of the radial distribution curves. The acceptable parameter field, is, however, slightly smaller in the case of the sector-visual method than in the case of the visual method using non-sectored plates (Fig. 2). However, the acceptable parameter fields are the same by the sector-visual and the sector-microphotometer methods. As can be expected, the average deviations from the mean $q_{\text{calcd}}/q_{\text{obsd}}$ for the best models decrease in the order visual > sector-visual > sector-microphotometer method. The sector-microphotometer method and the sector-visual method clearly distinguish the shoulders while the visual method does not. For comparison, the final parameters from the three methods are shown in Table IV.

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(13) J. W. Coutts and R. L. Livingston, THIS JOURNAL, **75**, 1542 (1953).

(14) L. S. Bartell, L. O. Brockway and R. H. Schwendeman, *J. Chem. Phys.*, **23**, 1854 (1955).

(15) A. H. Compton and S. K. Allison, "X-Rays in Theory and Experiment," D. Van Nostrand Co., Inc., New York, N. Y., 1935.

TABLE II

QUANTITATIVE ELECTRON DIFFRACTION DATA FOR VINYLIDENE CHLORIDE

Feature			$q_{calcd.}/q_{obsd.}$ Sector-microphotometer method				Sector-visual method	Visual method
Max.	Min.	$q_{obsd.}$	G	L	F	Y	G	G
3		15.9	0.989	0.984	0.994	0.981	0.980	0.978
	3	20.0	0.990	.985	0.995	.965	.983	.982
4		23.5	1.000	.987	1.009	.987	.994	.994
	4	26.8	1.000	.989	1.007	.989	.991	.991
5		29.7	0.993	.987	1.003	.990	.981	.980
	5	33.5	.993	.979	1.000	.967	.987	.987
6		37.8	.989	.984	1.000	.971	.995	.995
	6	42.3	.991	.979	0.993	.979	1.009	1.010
7		..	...	...	...	...	...	0.999
8		50.6	.982	.976	0.988	.962	0.981	.981
	8	54.7	.993	.978	1.005	.973	.995	.995
9		..	...	...	...	...	.988	.998
10		62.5	.998	.986	1.000	.979	.983	.983
	10	67.3	.984	.975	0.999	.970	.993	.993
11		71.4	.985	.976	.996	.972	.991	.991
	11	74.0	.991	.986	.999	.985	.986	.986
12		76.8	.997	.991	1.004	.984	.988	987
	12	80.9	.991	.980	0.999	.973	.991	.992
13		84.4	.993	.986	1.004	.982	.992	.992
	13	89.0	.985	.980	0.997	.974	.994	.994
14		..	...	...	...	...	.995	.996
	14	..	...	...	...	...	.992	.992
15		..	...	...	...	...	.989	.989
	15	..	...	...	...	...	.996	.997
16		..	...	...	..	...	1.001	1.002
17		..	...	...	...	...	0.996	0.996
18		..	...	...	...	...	1.004	...
Mean			0.991	0.983	1.000	0.976	0.991	0.992
Av. dev.			0.004	0.004	0.004	0.008	0.005	0.006

TABLE III

PARAMETERS FOR ACCEPTABLE MODELS

Parameter	L	G	F	Y
∠ClCCl, deg.	114	115	115	114
C–C, Å.	1.317	1.328	1.340	1.308
C–Cl, Å.	1.710	1.705	1.700	1.718

It is interesting to compare the results obtained in this investigation with those reported by earlier investigators.[4] A value of 1.69 ± 0.02 Å. was obtained for the C–Cl distance in earlier work as opposed to the value of 1.710 ± 0.010 Å. determined here. It will be noted that the newer value is within the experimental uncertainty of the earlier work. The experimental value of 1.324 ± 0.020 Å. determined here for the C–C distance indicates that the assumed value of 1.38 Å. in the older investigation must have been in error, thus furnishing one possible reason for the difference in the C–Cl distance.

TABLE IV

FINAL PARAMETERS OF VINYLIDENE CHLORIDE BY THE DIFFERENT METHODS

Parameter	Visual	Sector-visual	Sector-microphotometer
∠ClCCl, deg.	114.5 ± 1	114.5 ± 1	114.5 ± 1
C–Cl, Å.	1.71 ± 0.02	1.71 ± 0.01_5	1.710 ± 0.010
C–C, Å.	1.32 ± 0.03	1.32 ± 0.02_5	1.324 ± 0.020

The earlier work[4] indicated that the C–Cl distances for vinyl chloride and the three dichloroethenes were substantially the same. Results obtained in this Laboratory,[16,17] however, show a C–Cl distance of 1.74 ± 0.01 Å. for vinyl chloride and of 1.71 or 1.72 Å. (with uncertainties of ± 0.010 Å.) for the three dichloroethenes. For trichloroethene[18] and tetrachloroethene,[19] the C–Cl distances have been reported to be 1.72 ± 0.02 Å. and 1.72 ± 0.01 Å., respectively. These results indicate no regular trend in the C–Cl distances for the chloroethenes. Also, no trend is apparent in the C–C distance in these compounds.

The CCCl angle affords an interesting basis for comparison of the present and other investigations. The CCCl angle in vinyl chloride has been found[16] to be 119.5 ± 1.5°. The three dichloroethenes have substantially the same angle, 123.0 ± 1.5°, 123.0 ± 1° and 122.8 ± 0.5° for the *cis*-[17], *trans*-[16] and 1,1-dichloroethene, respectively. Values of 124.0 ± 2° and 121.5 ± 1° are reported for trichloroethene,[18] indicating different angles in the situations in which one and two chlorine atoms, respectively, are attached to the carbon atoms within the same molecule. The angle of 123.5° reported for tetrachloroethene[19] is in approximate agreement with the angles in the dichloroethenes.

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(16) L. H. Kaplan, Ph.D. Thesis, Purdue University, 1958.

(17) C. W. W. Hoffman, Ph.D. Thesis, Purdue University, 1957.

(18) W. N. Lipscomb (as reported by P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950)).

(19) I. L. Karle and J. Karle, *J. Chem. Phys.*, **20**, 63 (1952).

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