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# The Electron Diffraction Investigation of Phosgene, the Six Chloroethylenes, Thiophosgene, α-Methylhydroxylamine and Nitromethane[1]

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## Introduction

The importance of the use of interatomic distances as a test for resonance of molecules among several valence-bond structures has been mentioned in earlier papers,[2] in which it was pointed out that the interatomic distance for two bonded atoms in a resonating molecule is determined mainly by the strongest of the bonds between the two atoms provided by the resonating structures. We have now obtained evidence regarding the quantitative dependence of interatomic distance on bond type for resonance between a single bond and a double bond, and have made use of this relation in the discussion of the electronic structure of a number of molecules involving single bond–double bond resonance. The investigation is based largely on the determination of the atomic configuration of molecules by the diffraction of electrons; the description of this work is given in this paper, and the interpretation and discussion of results in the following one.

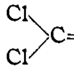
· Electron diffraction photographs of the gas molecules investigated were prepared in the usual way,[3] with film distances of about 12, 20 or 30 cm., the electron wave lengths being about 0.06 Å. The photographs were measured on a comparator and interpreted both by the radial distribution method[4] and the usual visual method.[5] The results are given below; in each case the interatomic distances and bond angles are provided with estimated probable errors, which indicate the extent to which we consider them to be reliable.

We are indebted to Dr. S. Weinbaum and Dr. J. Sherman for aid in connection with the extensive calculations involved in the interpretation of the photographs.

**Phosgene.**—The phosgene used was prepared by the action of fuming sulfuric acid on carbon tetrachloride in the presence of a catalyst (infusorial earth), and was purified by distillation.

The photographs show eight rings, with values of $s = (4\pi \sin \Theta/2)/\lambda$ (averages for eleven photographs measured by two observers) and estimated intensities given in Table I.

The eight-term radial distribution function (Fig. 1) shows two peaks, the first, with maximum at 1.79 Å., representing C–Cl, and the second, a broad peak with maximum at 2.74 Å., representing Cl–Cl and Cl–O (unresolved).

In applying the usual visual method we calculated curves for sixteen plane symmetric models. Three parameters are involved, the Cl–C–Cl angle, the C–O distance, and the C–Cl distance, the qualitative appearance of the curves being dependent on the angle and the ratio of the distances. The angle was varied from 110 to 125° and the ratio C–Cl/C–O from 1.23 to 1.60. Most of the models are eliminated at once by qualitative comparisons. The model corresponding to the valence bond structure  $Cl_2C{=}O$, with C–Cl = 1.76, C–O = 1.28, and the angle Cl–C–Cl = 110°, leads to curve A of Fig. 2, which is unsatisfactory in regard to the fourth and sixth rings, each of which is observed to be close to the preceding one. Curve B of Fig. 2 represents the model (with C–O = 1.12, C–Cl = 1.80, angle Cl–C–Cl = 110°) reported by Dornte[6] as the result of the study of electron diffraction photographs showing only four rings; it is seen that this curve is unsatisfactory, showing no maximum corresponding to our observed fourth ring.

It was found that models with the Cl–C–Cl angle equal to about 117° and the ratio of distances C–O/C–Cl equal to about 1.28/1.66 lead to curves in reasonably good qualitative agreement with experiment, all other models tried being unsatisfactory. Thus in Fig. 3 the curve for $\alpha$ = 117° (C) is reasonably satisfactory, the fourth and sixth rings being represented by humps rather than maxima; the curve for $\alpha$ = 115° (D) shows no sign of the sixth ring, and that for 120° (B) is unsatisfactory with regard to the clearly ob-

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[1] Some of the results communicated in this paper were presented at the meeting of the A. A. A. S. in Berkeley, June, 1934.

[2] L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293, 498 (1932); L. O. Brockway, *ibid.*, **19**, 860 (1930); L. O. Brockway and L. Pauling, *ibid.*, **19**, 868 (1933); L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

[3] R. Wierl, *Ann. Physik*, **8**, 521 (1931); L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.*, **19**, 69 (1933).

[4] L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

[5] See L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[6] R. W. Dornte, THIS JOURNAL, **55**, 4126 (1933).

TABLE I

PHOSGENE, $COCl_2$

| Max. | Min. | I | s | Values of x C | Values of x D | Values of x F | Values of C–Cl C | Values of C–Cl D | Values of C–Cl F |
|---|---|---|---|---|---|---|---|---|---|
| 1 | | 20 | 3.00 | 2.88 | 2.84 | 2.90 | (1.574 Å.) | (1.590 Å.) | (1.605 Å.) |
| | 2 | | 3.95 | 3.88 | 3.83 | 3.88 | (1.610) | (1.629) | (1.631) |
| 2 | | 15 | 5.05 | 5.15 | 5.07 | 5.11 | 1.672 | 1.687 | 1.680 |
| | 3 | | 6.33 | 6.50 | 6.35 | 6.40 | 1.684 | 1.685 | 1.678 |
| 3 | | 10 | 7.44 | 7.70 | 7.66 | 7.74 | 1.697 | 1.730 | 1.727 |
| | 4 | | 8.53 | 8.90 | | 8.87 | 1.711 | | 1.726 |
| 4 | | 2 | 9.34 | 9.63 | | 9.30 | 1.691 | | 1.653 |
| | 5 | | 10.33 | 10.76 | 10.25 | 10.50 | 1.708 | 1.667 | 1.687 |
| 5 | | 5 | 11.51 | 12.25 | 11.75 | 11.95 | 1.745 | 1.715 | 1.723 |
| | 6 | | 12.54 | | | | | | |
| 6 | | 1 | 13.51[a] | | | | | | |
| | 7 | | 14.52 | 14.50 | 14.25 | 14.40 | 1.638 | 1.649 | 1.646 |
| 7 | | 3 | 15.70 | 16.00 | 15.62 | 15.76 | 1.671 | 1.671 | 1.666 |
| | 8 | | 16.94 | 17.38 | 16.88 | 17.12 | 1.683 | 1.674 | 1.678 |
| 8 | | 1 | 18.10 | 18.25 | 17.80 | 18.00 | 1.654 | 1.652 | 1.651 |
| | | | | | | Average | 1.687 Å. | 1.681 Å. | 1.683 Å. |

Model C: Cl–C–Cl = 117° C–O = 1.28 Å. C–Cl = 1.64 Å
D: Cl–C–Cl = 117° 1.28 1.68
F: Cl–C–Cl = 118° 1.28 1.66

Results: C–Cl = 1.68 ± 0.02 Å.
Cl–Cl = 2.87 ± .02 Å.
C–O = 1.28 ± .03 Å.
Angle Cl–C–Cl = 117 ± 2°
Angle Cl–C–O = 121°30′ ± 1°

[a] This ring or shelf does not appear as a maximum on the simplified theoretical curves for these models.

served fourth ring. The effect of changing the C–O/C–Cl ratio is shown by the lower four curves in Fig. 2. Of these the curves for 117°, 1.28/1.64, and 117°, 1.28/1.68, agree very well with the photographs in qualitative appearance except that the sixth ring is not quite so well represented as expected, appearing only as a shelf on the curves.

In the figures of this paper showing intensity curves the observed values of *s* for apparent maxima and minima are indicated by small vertical lines. In comparing these with the calculated intensity curves it must be borne in mind that a linear change of scale may be made; the indicated *s* values are shown in each case for the *x*/*s* ratio determined by quantitative comparison for the model finally accepted.

The results of the quantitative comparison of the photographs with the curves for three models are given in Table I. Bearing in mind the qualitative comparison, we write as the probable configuration of the phosgene molecule $\alpha = 117 \pm 2°$ (angle Cl–C–Cl), C–Cl = 1.68 ± 0.02 Å., C–O = 1.28 ± 0.03 Å., and Cl–Cl = 2.87 ± 0.02 Å.

The values of Dornte (whose work has been referred to above), $\alpha = 110 \pm 5°$, C–Cl = 1.80 ± 0.04 Å., and C–O = 1.12 ± 0.02 Å., we believe to be less accurate than the errors assigned to them indicate.

**Vinyl Chloride.**—Photographs of vinyl chloride (from the Carbide and Carbon Chemical Company) were taken with a film distance of 12.19 cm., (the same distance being used also for the other chloroethylenes). The photographs show about six rings: the first very weak, the second strong, the third and fourth medium, the fifth weak and the sixth very weak. In addition there is apparent a very weak ring or shelf be-

TABLE II

VINYL CHLORIDE

| Max. | Min. | I | s | x for model D | C–Cl |
|---|---|---|---|---|---|
| 2 | | 30 | 5.19 | 5.14 | 1.663 Å. |
| | 3 | | 6.45 | 6.48 | 1.687 |
| 3 | | 20 | 7.61 | 7.77 | 1.714 |
| Shelf | | 5 | 9.84 | | |
| | 4 | | 10.76 | 10.76 | 1.680 |
| 4 | | 15 | 12.15 | 12.21 | 1.687 |
| | 5 | | 13.51 | 13.48 | 1.676 |
| 5 | | 10 | 15.27 | 15.01 | 1.653 |
| 6 | | 5 | 19.10 | 19.40 | 1.707 |
| | | | | Average | 1.683 Å. |

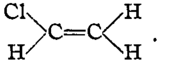
Results: C–C = 1.38 Å. (assumed)
$C_1$–Cl = 1.69 ± 0.02 Å.
$C_2$–Cl = 2.70 ± .02 Å.
$\alpha$ = 122 ± 2°

tween the third and fourth rings, somewhat closer to the third than to the fourth. Measured values of *s* obtained by two observers from nine photographs are given in the fourth column of Table II and estimated intensities for the rings in the third column.

The six-term radial distribution curve is given in Fig. 1. It shows two pronounced peaks, with maxima at 1.695 and 2.69 Å., with indication of a subsidiary peak at 1.35 or 1.40 Å. The first two we associate with the two carbon–chlorine interactions, and the last with carbon–carbon. If we accept the value 1.38 Å. for C–C, the distances 1.695 and 2.69 Å. lead to the value 121° for the C–C–Cl bond angle $\alpha$.

In applying the usual visual method, we have found that the photographs do not provide enough information to permit us to evaluate simultaneously the two distances C–Cl and C–C and the angle Cl–C–C with much accuracy. Accordingly we have assumed the C–C distance to have the double bond value 1.38 Å., and have calculated curves for C–Cl = 1.68, C–C = 1.38 and the angle $\alpha$ = 130, 125, 122.5 and 120°. These are shown as B, C, D and E in Fig. 4. Of these B and C are qualitatively unsatisfactory in that the hump corresponding to the faint ring or shelf observed between the third and fourth rings is too large, and E in that the hump is too small. Comparison of measured values of *s* with the *x* values for model D (Table II) leads to the carbon–chlorine distances 1.683 and 2.70 Å.

Combining the results of the two methods, we write C–C = 1.38 Å. (assumed), $C_1$–Cl = 1.69 ± 0.02 Å., $C_2$–Cl = 2.70 ± 0.02 Å., $\alpha$ = 122 ± 2°. No earlier electron diffraction work on this substance has been reported.

It is of interest to consider also the model with $C_1$–Cl = 1.76, C–C = 1.38 and $\alpha$ = 125°, corresponding to the non-resonating structure  $\mathrm{Cl(H)C{=}CH_2}$. This gives the curve A of Fig. 4, which is in satisfactory qualitative agreement with the photographs. The quantitative comparison leads to the distances C–Cl = 1.68 Å. and C–C = 1.32 Å., however, and since the latter distance should not fall below 1.38 Å., the experimentally established value for the carbon–carbon double bond, the non-resonating structure is unsatisfactory.

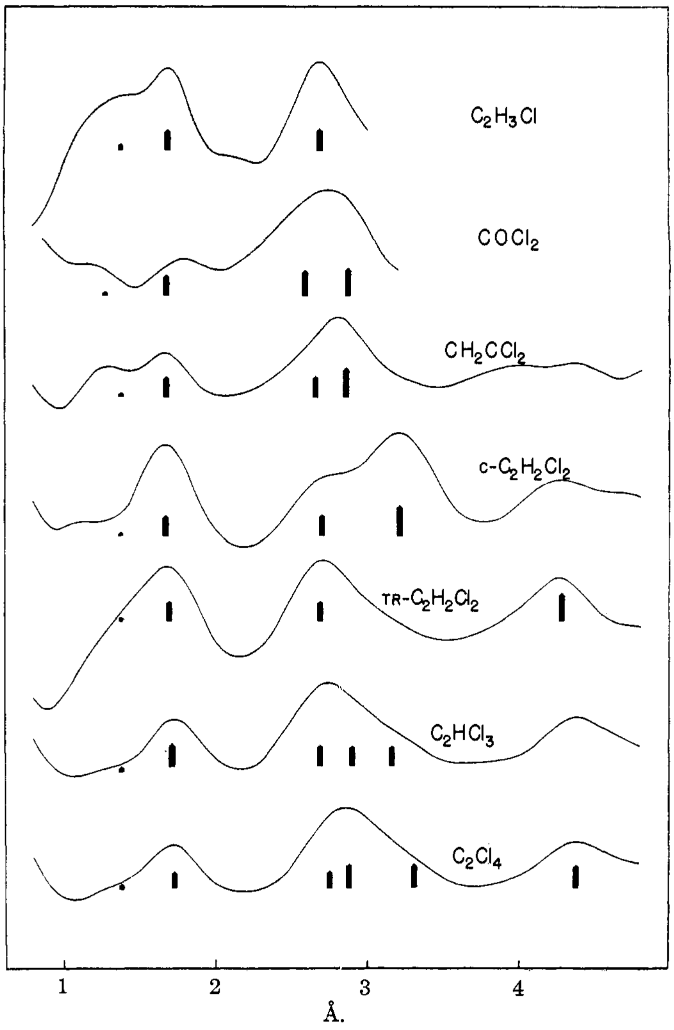


Fig. 1.—Radial distribution curves for phosgene and the six chloroethylenes.

**1,1-Dichloroethylene.**—The substance was prepared by treating 1,1,2-trichloroethane (made by passing vinyl chloride into antimony pentachloride) with alcoholic potassium hydroxide, and was purified by fractional distillation.

The photographs, showing seven well-defined rings, have the following qualitative appearance: the first medium, the second strong, the third medium, the fourth weak and the fifth medium weak, these five being about equally spaced; then a wide minimum and a weak ring, and another wide minimum and weak ring. Measured values of *s* (averages for four photographs) and estimates of *I* are given in Table III.

TABLE III

1,1-DICHLOROETHYLENE

| Max. | Min. | $I$ | $s$ | $x$ for Model C | $x$ for D | C–Cl for Model C | C–Cl for D |
|---|---|---|---|---|---|---|---|
| 1 | | 15 | 2.87 | 2.75 | 2.74 | (1.629 Å.) | (1.623 Å.) |
| | 2 | | 3.83 | 3.73 | 3.67 | (1.656) | (1.629) |
| 2 | | 40 | 5.02 | 4.96 | 4.95 | 1.679 | 1.676 |
| | 3 | | 6.28 | 6.23 | 6.20 | 1.687 | 1.679 |
| 3 | | 15 | 7.33 | 7.40 | 7.34 | 1.717 | 1.702 |
| | 4 | | 8.42 | 8.33 | 8.22 | 1.681 | 1.660 |
| 4 | | 8 | 9.38 | 9.24 | 9.15 | 1.674 | 1.659 |
| | 5 | | 10.52 | 10.50 | 10.33 | 1.697 | 1.670 |
| 5 | | 20 | 11.76 | 11.78 | 11.73 | 1.703 | 1.696 |
| 6 | | 10 | 15.55 | 15.75 | 15.56 | 1.722 | 1.701 |
| | | | | | Average C–Cl = | 1.695 Å. | 1.680 Å. |
| | | | | | Cl–Cl = | 2.858 Å. | 2.870 Å. |

Model C: C–Cl/C–C = 1.70/1.38, $\beta$ = 115°
Model D: C–Cl/C–C = 1.70/1.38, $\beta$ = 117.5°
Results: C–C = 1.38 Å. (assumed)
C–Cl = 1.69 ± 0.02 Å.
Cl–Cl = 2.86 ± 0.02 Å.
Angle Cl–C–Cl = 116 ± 2°
Angle Cl–C–C = 122 ± 1°

The six-term radial distribution function (Fig. 1) shows a C–Cl peak with maximum at 1.67 Å., and a large peak due to both Cl–Cl and C–Cl interactions. The lack of resolution of this peak (maximum at 2.81 Å.) makes its interpretation difficult.

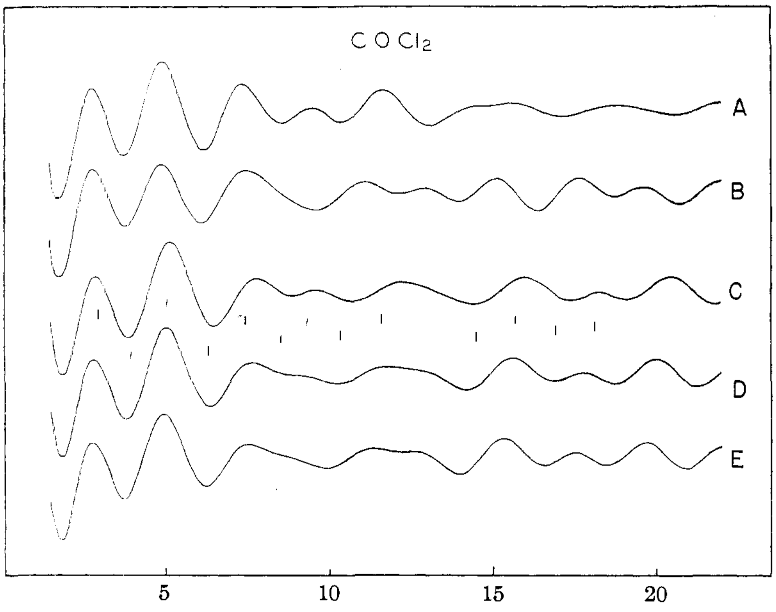
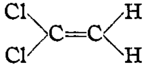


Fig. 2.—Simplified intensity curves for phosgene. A, $\alpha$ (angle Cl–C–Cl) = 110°, $r$ (ratio C–O/C–Cl) = 1.28/1.76; B, $\alpha$ = 110°, $r$ = 1.12/1.80; C, $\alpha$ = 117°, $r$ = 1.28/1.64; D, $\alpha$ = 117°, $r$ = 1.28/1.68; E, $\alpha$ = 117°, $r$ = 1.28/1.72.

We have calculated intensity curves for twelve models, with the Cl–C–Cl angle $\beta$ varied between 110 and 125° and the C–Cl/C–C ratio varied between 1.76/1.38 and 1.64/1.38. It was not found possible to evaluate the C–Cl/C–C ratio as well as the angle $\beta$ with much accuracy; accordingly we have assumed the C–C distance to have the double bond value 1.38 Å. Of the models tried, only those with $\beta$ equal to about 115° agree qualitatively with the photographs. For example, the model with C–Cl = 1.76 Å., C–C = 1.38 Å., and $\beta$ = 110°, corresponding to the valence-bond structure  $Cl_2C{=}CH_2$, is unsatisfactory in that the fourth maximum on the curve (curve A of Fig. 5) is higher than the third, whereas the fourth ring is observed to be much weaker than the third and fifth. Quantitative comparison with this and other curves shows the C–Cl distance to be about 1.70 Å. Curves B, C, D and E of Fig. 5 are calculated for C–Cl = 1.70, C–C = 1.38, and the angle $\beta$ = 112.5, 115, 117.5 and 120°, respectively. Of these curve B is unsatisfactory in that it shows an additional maximum between those corresponding to the fifth and sixth rings, and curve E in that the fourth maximum is too high. Curves C and D are satisfactory, and we accordingly accept for the Cl–C–Cl angle the value $\beta = 116 \pm 2°$.

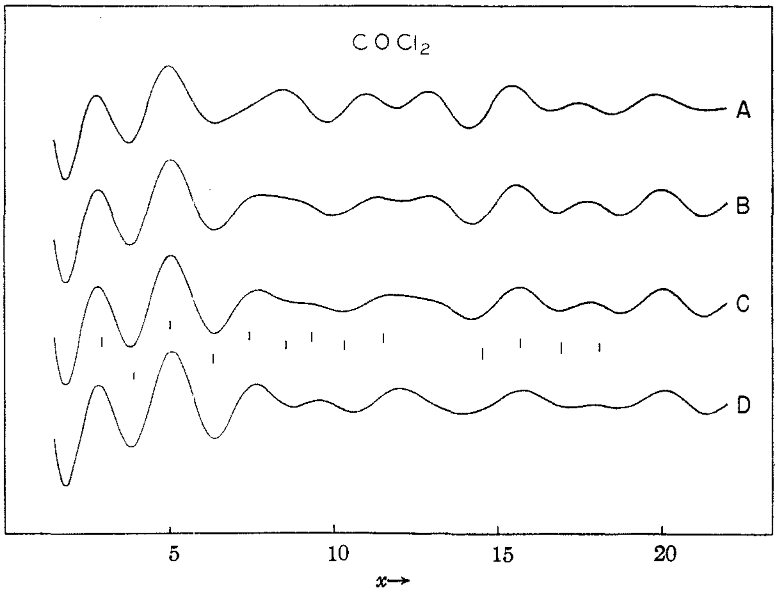


Fig. 3.—Intensity curves for phosgene, with $r$ = 1.28/1.68, and $\alpha$ = 125, 120, 117 and 115° for A, B, C and D, respectively.

The quantitative comparison of the measured values of $s$ and the $x$ values for models C and D, given in Table III, leads to the interatomic distances C–Cl = 1.69 ± 0.02 Å., Cl–Cl = 2.86 ± 0.02 A., with the angle Cl–C–Cl = 116 ± 2° and C–C = 1.38 Å. (assumed).

The only previous investigation of this substance, that of Wierl[7] by electron diffraction, gave the value Cl–Cl = 2.9 ± 0.3 Å.

**cis-Dichloroethylene.**—The sample of *cis*-dichloroethylene used was obtained from a mixture of the *cis* and *trans* compounds by fractional distillation with a 90-cm. column.

The photographs show five well-defined rings, with the following qualitative appearance: the first ring medium; the second strong, with an outer shelf; the third medium; the fourth weak, and somewhat closer to the third than to the fifth; the fifth medium weak. Observed values of $s$ (averages for nine photographs) and estimated intensities are given in Table IV.

The six-term radial distribution function is shown in Fig. 1. It shows two well-defined peaks, with maxima at 1.67 Å. (C–Cl) and 3.21 Å. (Cl–Cl). These correspond to the value 123°15′ for the angle Cl–C–C, and to another C–Cl distance of 2.69 Å., some indication of which is visible in the curve.

On calculation of theoretical intensity curves it was found that all models giving rough qualitative agreement with the photographs lead to a Cl–Cl distance close to 3.23 Å. In order to determine the C–Cl distance, curves were calculated for a series of models with C–C = 1.38 and Cl–Cl = 3.23, the value of C–Cl being varied. It was found that the shelf beyond the second ring changes rapidly in this series; only for C–Cl = 1.68 (curve C in Fig. 6) does the shelf correspond to its appearance on the photograph (about one-fourth as pronounced as the second ring). Decrease by 3% wipes it out entirely. We accordingly accept model C. The comparison of observed $s$ values and $x$ values for this model, given in Table IV, leads to C–Cl = 1.671 Å., Cl–Cl = 3.223 Å.

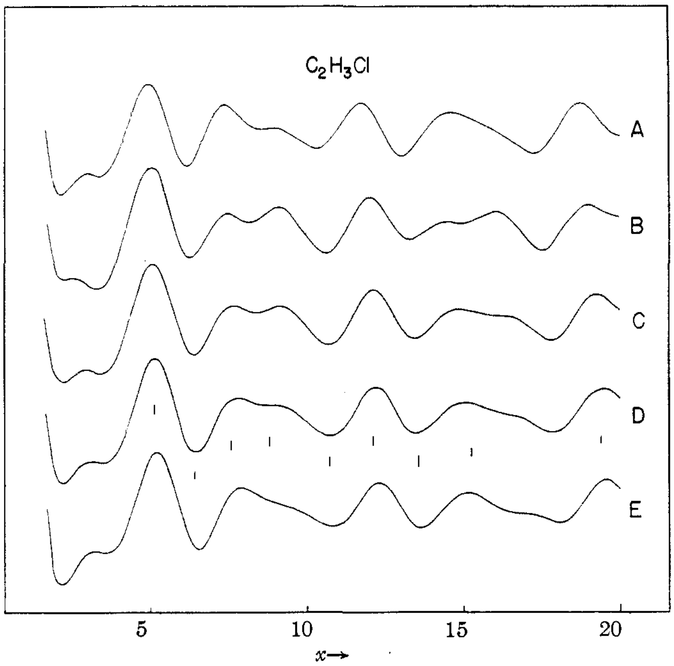


Fig. 4.—Intensity curves for five models of vinyl chloride.

Curve A, calculated for the non-resonating

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(7) R. Wierl, *Ann. Physik*, **13**, 453 (1932).

Table IV

*cis*-Dichloroethylene

| Max. | Min. | $I$ | $s$ | $x$ for Model A | $x$ for C | C–Cl for Model A | C–Cl for C |
|---|---|---|---|---|---|---|---|
| 1 | | 10 | 2.480 | 2.36 | 2.46 | (1.675 Å.) | (1.666 Å.) |
| | 2 | | 3.489 | 3.20 | 3.35 | (1.614) | (1.613) |
| 2 | | 30 | 4.652 | 4.33 | 4.62 | (1.639) | (1.668) |
| Shelf | | 8 | 6.00 | | | | |
| | 3 | | 6.958 | 6.57 | 6.88 | 1.662 | 1.661 |
| 3 | | 20 | 8.095 | 7.74 | 8.14 | 1.682 | 1.689 |
| | 4 | | 9.22 | 8.78 | 9.23 | 1.675 | 1.681 |
| 4 | | 3 | 10.10 | 9.62 | 10.01 | 1.677 | 1.665 |
| | 5 | | 11.16 | 10.54 | 10.98 | 1.664 | 1.653 |
| 5 | | 10 | 12.17 | 11.63 | 12.15 | 1.682 | 1.677 |
| | | | | | | Average 1.674 Å. | 1.671 Å. |

Model A: C–C = 1.38, C–Cl = 1.76, $\beta$ = 125°
Model C: C–C = 1.38, C–Cl = 1.68, $\beta$ = 123.7°
Results: C–C = 1.38 Å. (assumed)
C–Cl = 1.67 ± 0.03 Å.
Cl–Cl = 3.22 ± 0.02 Å.
Angle Cl–C–C = 123.5 ± 1°

model with the Cl–C–C angle $\beta$ = 125°, C–C = 1.38, and C–Cl = 1.76, is in satisfactory qualitative agreement with the photographs, quantitative comparison, however, giving C–Cl = 1.674 Å. and Cl–Cl = 3.233 Å. (Table IV), the only essential difference from the results for model C being in the C–C distance, for which the low value 1.30 Å. is obtained. Curve D, calculated for $\beta$ = 130°, C–Cl = 1.72, and C–C = 1.38, shows the extreme qualitative disagreement caused by a relatively small change in model.

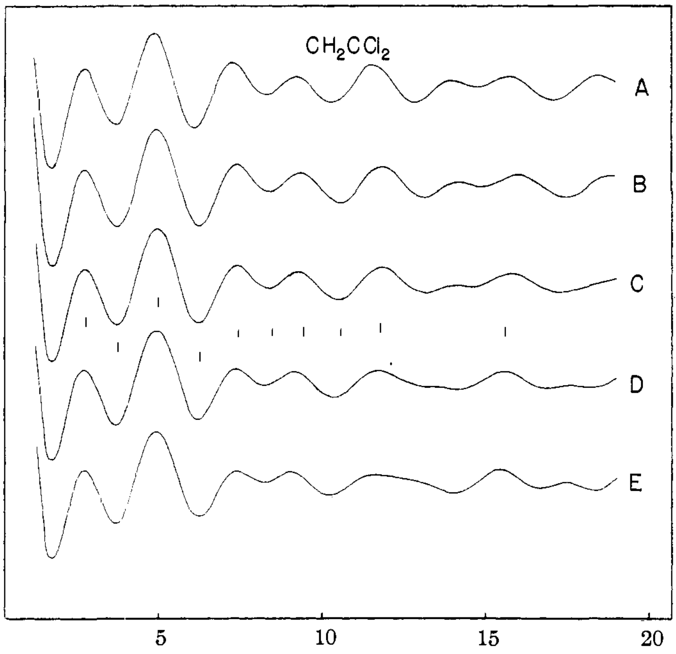

Fig. 5.—Intensity curves for 1,1-dichloroethylene.

Combining the results of the two methods, we accept for the structural constants the values C–C = 1.38 Å. (assumed), C–Cl = 1.67 ± 0.03 Å., Cl–Cl = 3.22 ± 0.02 Å., $\beta$ (angle Cl–C–C) = 123.5 ± 1°. Previous investigations have given the less accurate values Cl–Cl = 3.30 ± 0.1 Å. (Wierl,[7] electron diffraction) and Cl–Cl = 3.6 Å. (Debye,[8] x-ray diffraction).

**trans-Dichloroethylene.**—The sample of *trans*-dichloroethylene was separated from a mixture with the *cis* compound by fractional distillation.

The photographs show seven measurable rings, with apparent intensities as given in Table V (the second ring showing an outer shelf). Values of $s$ (averages for ten photographs) are also given in the table for the features which could be measured with accuracy.

The eight-term radial distribution function, given in Fig. 1, shows three well-defined peaks, with maxima at 1.675, 2.70 and 4.27 Å. These we correlate with the two C–Cl interactions and the Cl–Cl interaction, the three interactions being of about equal importance. The distances correspond to the values C–C = 1.38 Å., $\beta$ (angle Cl–C–C) = 123°.

In applying the usual visual method we observed that the quantitative comparison with the photographs of all the models tried gave values close to 4.27 Å. for the Cl–Cl distance. We then

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(8) P. Debye, *Physik. Z.*, **31**, 142 (1930).

TABLE V

*trans*-DICHLOROETHYLENE

| Max. | Min. | | *s* | *x* for Model C | D | C–Cl for Model C | D |
|---|---|---|---|---|---|---|---|
| 1 | | 5 | 3.11 | 3.25 | 3.26 | (1.777 Å.) | (1.803 Å.) |
| | 2 | | 3.98 | 3.95 | 3.95 | 1.687 | 1.707 |
| 2 | | 20 | 4.90 | 4.87 | 4.87 | 1.690 | 1.716 |
| Shelf | | 5 | 5.68 | | | | |
| | 3 | | 6.78 | 6.71 | 6.77 | 1.682 | 1.717 |
| 3 | | 10 | 7.74 | 7.75 | 7.74 | 1.702 | 1.720 |
| 4 | | 1 | 9.18 | 9.17 | 9.18 | 1.698 | 1.720 |
| 5 | | 1 | 10.59 | 10.63 | 10.62 | 1.706 | 1.724 |
| 6 | | 5 | 12.11 | 12.10 | 12.11 | 1.699 | 1.720 |
| 7 | | 2 | 14.97 | 15.05 | 15.02 | 1.709 | 1.725 |
| | | | | | Average C–Cl | 1.697 Å. | 1.719 Å. |
| | | | | | Cl–Cl | 4.272 Å. | 4.277 Å. |

Results:
C–C = 1.38 Å. (assumed)
C–Cl = 1.69 ± 0.02 Å.
Cl–Cl = 4.27 ± 0.02 Å.
Angle Cl–C–C = 122.5 ± 1°

calculated curves for models with Cl–Cl = 4.28, C–C = 1.38, and C–Cl = 1.68, 1.70, 1.72 and 1.76 (curves B, C, D and E, respectively, of Fig. 7). All of these agree qualitatively with the photographs except in so far as the weak fourth and fifth rings are concerned; the approximate equality of these rings is best represented by curve D. The results of the quantitative comparison for C and D are given in Table V; it is seen that the value of the Cl–Cl distance is essentially independent of the model.

Averaging the results of the two methods, with about equal weights, we assign to the structural parameters the values C–C = 1.38 Å. (assumed), C–Cl = 1.69 ± 0.02 Å., Cl–Cl = 4.27 ± 0.02 Å., β (angle Cl–C–C) = 122.5 ± 1°. Previous studies gave the values Cl–Cl = 4.33 ± 0.1 Å. (Wierl,[7] electron diffraction) and Cl–Cl = 4.1 Å. (Debye,[8] x-ray diffraction). In addition a note has been published by de Laszlo[9] in which the C–Cl distance in this molecule is given as 1.74 Å.

**Trichloroethylene.**—The photographs of trichloroethylene (Eastman) show six rings, with intensities weak, strong, medium, weak, medium weak, weak. Characteristic features are that there is some indication of a small shelf between the second and third rings (closer to the second than to the third) and that the weak fourth ring is closer to the third than to the fifth. The measured values of *s* (average for three photographs, two observers) are given in Table VI.

The five-term radial distribution function (Fig. 1) shows three peaks, with maxima at 1.73, 2.85 and 4.37 Å., the first corresponding to the small C–Cl distances, the second to the larger C–Cl distances and to two Cl–Cl distances, and the third to the *trans* Cl–Cl distance. The lack of resolution of the second peak makes it of little value.

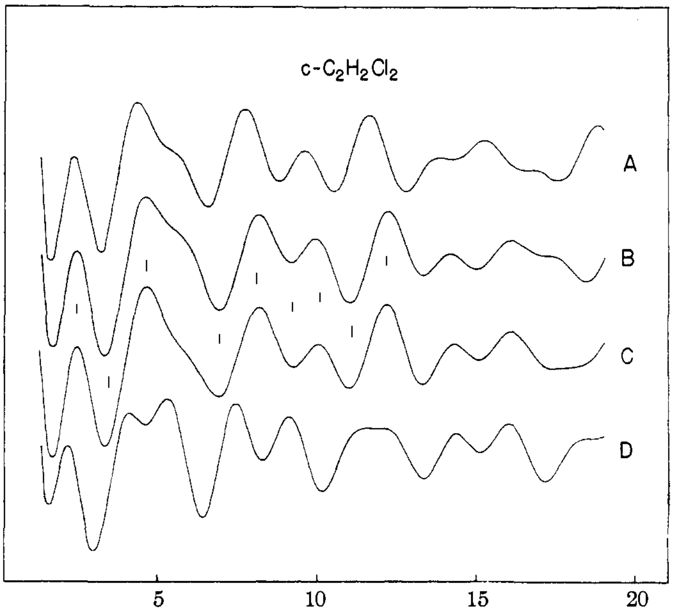

Fig. 6.—Intensity curves for *cis*-dichloroethylene.

In discussing the possible molecular models we have restricted ourselves mainly to those in which

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(9) H. de Laszlo, *Nature*, **136**, 474 (1935).

the three Cl–C–C angles are equal. Curve A (Fig. 8) is calculated for C–C = 1.38, C–Cl = 1.76 and the angles Cl–C–C = 125° for the $CCl_2$ group and 123° for the CHCl group. This curve agrees with the photographs qualitatively, and leads on quantitative comparison to the value 1.69 Å. for C–Cl (and hence 1.32 Å. for C–C).

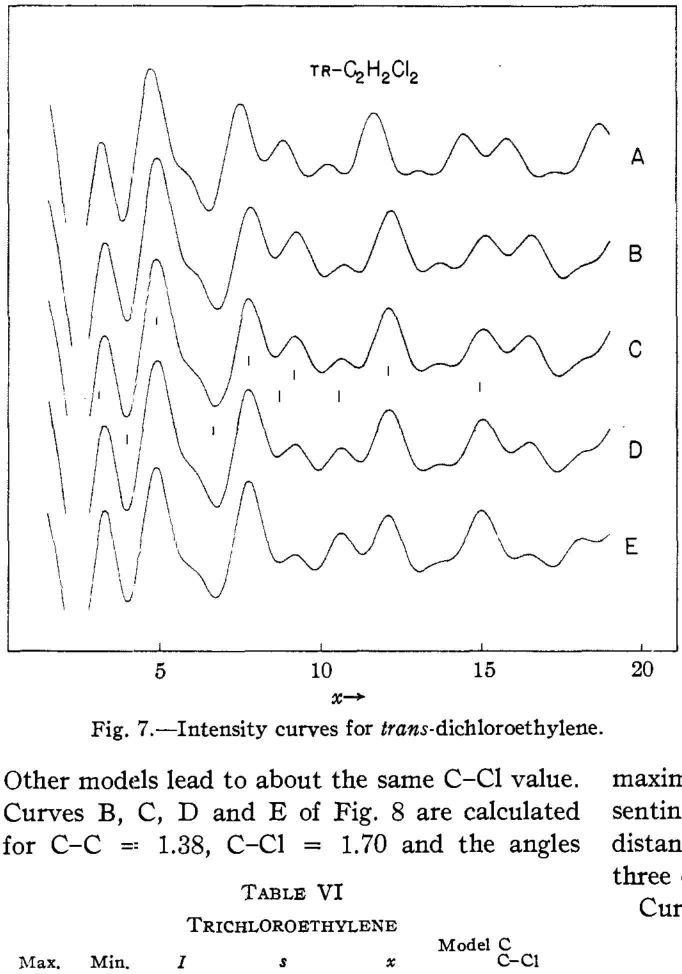

Fig. 7.—Intensity curves for *trans*-dichloroethylene.

Other models lead to about the same C–Cl value. Curves B, C, D and E of Fig. 8 are calculated for C–C = 1.38, C–Cl = 1.70 and the angles Cl–C–C = 125, 122.5, 121.5 and 120°, respectively. Of these curves C alone is in satisfactory qualitative agreement with the photographs. Quantitative comparison (Table VI) leads to the values C–Cl = 1.69 Å., Cl–Cl = 2.85, 3.19 and 4.27 Å. Giving somewhat more weight to these than to the radial distribution values, we accept as representing the configuration of the molecule the values C–C = 1.38 Å. (assumed), C–Cl = 1.71 ± 0.03 Å., Cl–Cl = 2.72 ± 0.04 Å. (in the $CCl_2$ group), and Cl–Cl = 3.23 ± 0.05 Å. and 4.33 ± 0.05 Å. (between $CCl_2$ and CHCl), with the angles Cl–C–C = 123 ± 2°.

Table VI

Trichloroethylene

| Max. | Min. | I | s | Model C x | C–Cl |
|---|---|---|---|---|---|
| 1 | | | 2.91 | 2.80 | (1.639 Å.) |
| | 2 | | 3.88 | 3.73 | (1.633) |
| 2 | | 30 | 4.86 | 4.79 | 1.675 |
| | 3 | | 6.43 | | |
| 3 | | 15 | 7.81 | 7.73 | 1.683 |
| | 4 | | 8.68 | 8.59 | 1.682 |
| 4 | | 4 | 9.67 | 9.11 | 1.602 |
| | 5 | | 10.91 | 10.97 | 1.709 |
| 5 | | 10 | 12.04 | 12.03 | 1.699 |
| 6 | | 4 | 15.49 | 16.20 | 1.778 |
| | | | | Average | 1.690 Å. |

Results: C–C = 1.38 Å. (assumed)
C–Cl = 1.71 ± 0.03 Å.
Cl–Cl = 2.72 ± 0.04 Å.
3.23 ± 0.05 Å.
4.33 ± 0.05 Å.
Angles Cl–C–C = 123 ± 2°

Trichloroethylene previously has been studied by this method by Dornte,[10] who reported the values C–C = 1.32 ± 0.08 Å., C–Cl = 1.82 ± 0.08 Å., Cl–Cl = 3.41 ± 0.08 Å., and Cl–Cl = 4.52 ± 0.08 Å., in approximate agreement with our values.

**Tetrachloroethylene.**—The rather weak photographs of tetrachloroethylene (Eastman) obtained at room temperature show six rings, the first medium, the second strong, the third medium, the fourth weak, the fifth medium weak and the sixth weak. Averaged values of *s* (for four photographs) and estimated intensities are given in Table VII.

The six-term radial distribution function (Fig. 9) shows three peaks, with maxima at 1.72, 2.86 and 4.37 Å., the first representing a C–Cl distance, the third the *trans* Cl–Cl distance, and the large second peak representing three distances.

Curves A, B, C and D of Fig. 9 are calculated

Table VII

Tetrachloroethylene

| Max. | Min. | I | s | x for model B | C–Cl |
|---|---|---|---|---|---|
| 1 | | 15 | 2.78 | 2.70 | (1.69 Å.) |
| | 2 | | 3.81 | 3.68 | (1.68) |
| 2 | | 30 | 4.76 | 4.63 | 1.691 |
| 3 | | 10 | 7.46 | 7.52 | 1.753 |
| 4 | | 3 | 9.00 | 9.12 | 1.761 |
| 5 | | 8 | 11.84 | 11.72 | 1.722 |
| 6 | | 3 | 15.17 | | |
| | | | | Average | 1.732 Å. |

Results: C–C = 1.38 Å. (assumed)
C–Cl = 1.73 ± 0.02 Å.
Cl–Cl = 2.87 ± 0.03 Å.
3.30 ± 0.03 Å.
4.28 ± 0.03 Å.
Angle Cl–C–C = 123° 45′ ± 1°

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(10) R. W. Dornte, *J. Chem. Phys.*, **1**, 566 (1933).

for models with C–C = 1.38, C–Cl = 1.74 and the angles Cl–C–C = 125°, 123°45′, 122°30′ and 121°15′, respectively. It is seen that the curves

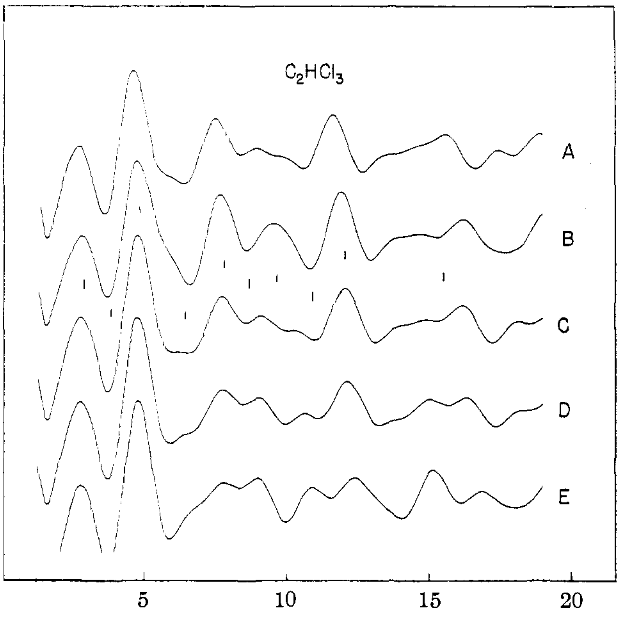

Fig. 8.—Intensity curves for trichloroethylene.

change very rapidly with change in angle. The appearance of the photograph is closely reproduced by curve B, and not so well by C or A; the latter is unsatisfactory only in that the fourth peak is not sufficiently displaced toward the third. We accordingly accept for the Cl–C–C angle the value 123°45′ ± 1°.

The quantitative comparison leads to C–Cl = 1.732 Å. and Cl–Cl (*trans*) = 4.38 Å., in essential agreement with the results of the radial distribution treatment. We accordingly accept for the structural parameters of the molecule the values C–C = 1.38 Å. (assumed), C–Cl = 1.73 ± 0.02 Å., Cl–Cl = 2.87 ± 0.03 Å. (in the same $CCl_2$ group), and Cl–Cl = 3.30 ± 0.03 Å. and 4.28 ± 0.03 Å. (between $CCl_2$ groups), with the angle Cl–C–C = 123°45′ ± 1°.

A previous electron diffraction investigation by Dornte[10] gave the values C–C = 1.32 ± 0.08 Å., C–Cl = 1.82 ± 0.08 Å., and Cl–Cl = 3.41 ± 0.08 Å. and 4.52 ± 0.08 Å., in approximate agreement with our results. De Laszlo has also reported the value C–Cl = 1.74 Å. in a preliminary note.[9]

**Thiophosgene.**—The thiophosgene used was prepared by the chlorination of carbon disulfide and subsequent reduction, and purified by fractional distillation.[11]

The photographs show nine rings, for which measured *s* values and estimated intensities are given in Table VIII (averages for four photo-

TABLE VIII

THIOPHOSGENE

| Max. | Min. | *I* | *s* | *x* for model B | C–Cl |
|---|---|---|---|---|---|
| 1 | | 10 | 2.84 | 2.67 | (1.598 Å.) |
| | 2 | | 3.75 | 3.67 | (1.664) |
| 2 | | 25 | 5.00 | 4.84 | (1.646) |
| | 3 | | 6.08 | 6.04 | 1.689 |
| 3 | | 12 | 7.16 | 7.13 | 1.693 |
| | 4 | | 8.10 | 8.06 | 1.692 |
| 4 | | 12 | 9.17 | 9.09 | 1.685 |
| | 5 | | 10.25 | 10.29 | 1.707 |
| 5 | | 6 | 11.40 | 11.49 | 1.713 |
| | 6 | | 12.43 | 12.51 | 1.711 |
| 6 | | 3 | 13.41 | 13.48 | 1.709 |
| | 7 | | 14.51 | 14.56 | 1.706 |
| 7 | | 3 | 15.56 | 15.75 | 1.721 |
| | 8 | | 16.78 | 16.88 | 1.710 |
| 8 | | 1 | 17.79 | 17.90 | 1.711 |
| | 9 | | 18.90 | 18.87 | 1.697 |
| 9 | | 1 | 19.90 | 19.97 | 1.706 |
| | | | | Average | 1.704 Å. |

Results: C–S = 1.63 Å. (assumed)
Angle Cl–C–Cl = 116 ± 2° (assumed)
C–Cl = 1.70 ± 0.02 Å.
Cl–Cl = 2.88 ± 0.04 Å.
Cl–S = 2.90 ± 0.04 Å.

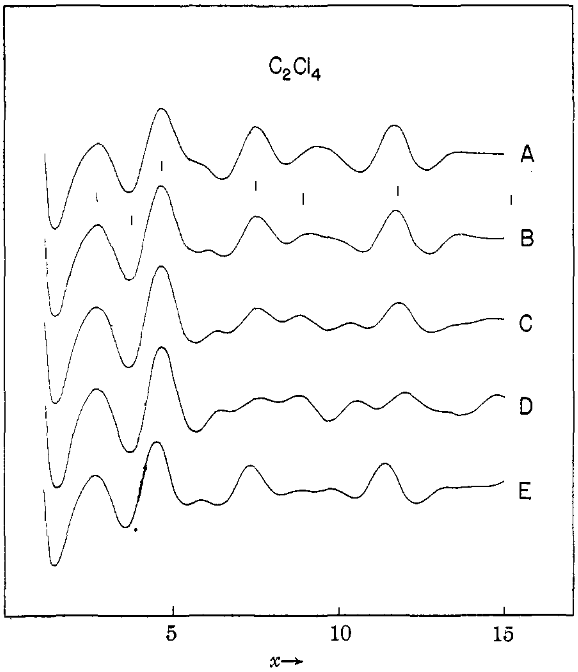

Fig. 9.—Intensity curves for tetrachloroethylene.

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[11] "Organic Syntheses," John Wiley and Sons, Inc., New York City Coll., Vol. I, p. 493.

graphs[12]). The nine-term radial distribution curve (Fig. 10) shows two well-defined peaks, the first, with maximum at 1.59 Å., corresponding to the C–S and C–Cl distances, and the second, with maximum at 2.87 Å., to the Cl–Cl and Cl–S distances. The sharpness of the second peak (which closely resembles the Cl–Cl peak for carbon tetrachloride) indicates strongly that the Cl–Cl and Cl–S distances are nearly equal. The position of the first maximum is unreliable, being strongly dependent on the estimated intensity values.

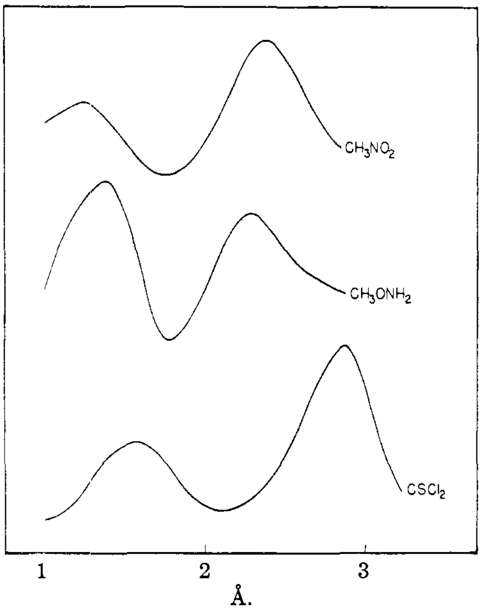

Fig. 10.—Radial distribution curves for nitromethane, α-methylhydroxylamine and thiophosgene.

On calculating simplified intensity curves for eight models it was found that all of the parameters determining the structure of the molecule could not be evaluated. The curves out to the tenth ring are affected very little by small changes in the Cl–Cl/Cl–S ratio, no perceptible differences existing between those calculated for C–S = 1.63, C–Cl = 1.70, and the angle Cl–C–Cl = 114, 116, 118 and 120°, respectively, the Cl–Cl/Cl–S ratio changing from 0.97 to 1.02. All of these curves agree satisfactorily with the photographs in qualitative appearance; the 116° curve is shown as A in Fig. 11. The curves are also not very sensitive to small changes in the position of the light carbon atom; however, the curve for C–Cl = 1.76, C–S = 1.44 and the angle Cl–C–Cl = 110° (B of Fig. 11) is qualitatively unsatisfactory in regard to the fourth ring, which is observed to be as strong as the third.

We have assumed for the C–S distance the double bond value 1.63 Å., as given by the table of covalent radii (and verified by the value 1.64 Å. reported for crystals of thiourea),[13] and for the angle Cl–C–Cl the value 116 ± 2°, as in phosgene and 1,1-dichloroethylene. The observed size of the Cl–Cl–S triangle then requires that C–Cl be close to 1.70 Å. The quantitative comparison with curve A leads to C–Cl = 1.704 Å.; taking some cognizance of the 2.87 Å. peak on the radial distribution curve, we accept for the structural parameters the values C–S = 1.63 Å. (assumed), angle Cl–C–Cl = 116 ± 2° (assumed), C–Cl = 1.70 ± 0.02 Å., Cl–Cl = 2.88 ± 0.04 Å., and Cl–S = 2.90 ± 0.04 Å.

**α-Methylhydroxylamine.**—The photographs of α-methylhydroxylamine (Eastman) show three well-defined rings, with *s* values (average for four films) and estimated intensities given in Table IX. The three-term radial distribution function (Fig. 10) shows peaks with maxima at 1.39 and 2.31 Å. The first we interpret as showing the C–O and O–N distances, unresolved, the table of covalent radii giving for them the values 1.43 and 1.36 Å., respectively. The C–N distance 2.31 Å. then leads to the value 112° for the C–O–N angle.

Intensity curves were calculated for the following values of the angle: 114, 110 and 106°. In these the ratio of the O–N and C–O distances was taken as 1.36/1.43. The curves for the first two are shown in Fig. 12 and the *x* values in Table IX. Model A (110° angle) is superior to Model B (114° angle) as indicated by the poor agreement between the *x* and *s* values for the second maxi-

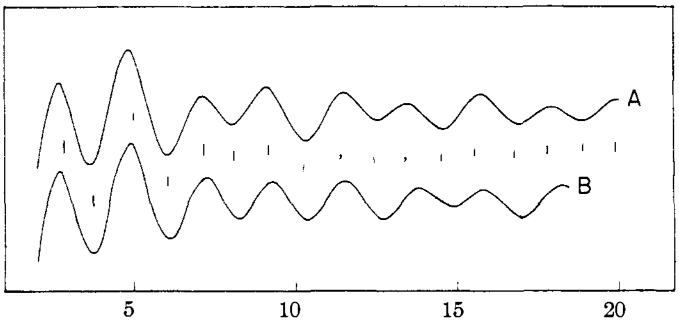

Fig. 11.—Intensity curves for thiophosgene.

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[12] Some measurements made on five rings of very weak photographs, disagreeing with those in the table by about 2%, were discarded.

[13] R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **81**, 386 (1932).

TABLE IX

$\alpha$-METHYLHYDROXYLAMINE

| Max. | Min. | $I$ | $s$ | Model A $x$ | Model A N–O | Model B $x$ | Model B N–O |
|---|---|---|---|---|---|---|---|
| 1 | | 5 | 6.00 | 6.10 | 1.383 Å. | 6.04 | 1.369 Å. |
| | 2 | | 7.95 | 7.93 | 1.357 | 7.88 | 1.349 |
| 2 | | 2 | 9.49 | 9.93 | 1.418 | 10.20 | (1.461) |
| | 3 | | 12.13 | 12.20 | 1.367 | 12.17 | 1.362 |
| 3 | | 1 | 13.94 | 14.30 | 1.393 | 14.18 | 1.381 |
| | | | | Average | 1.384 Å. | | 1.365 Å. |

Results: N–O = 1.37 ± 0.02 Å.
C–O = 1.44 ± 0.02 Å.
C–N = 2.31 ± 0.03 Å.
Angle C–O–N = 111 ± 3°

mum in Model B. The 106° model was rejected because it leads to widely fluctuating values for the size of the molecule as calculated from the various maxima and minima. The quantitative comparison for Model A leads to N–O = 1.38 Å., C–O = 1.45 Å. and C–N = 2.31 Å.

Combining the results of the two methods we obtain the values N–O = 1.37 ± 0.02 Å., C–O = 1.44 ± 0.02 Å., angle C–O–N = 111 ± 3°, C–N = 2.31 ± 0.03 Å.

**Nitromethane.**—The photographs of nitromethane (Eastman) show four well-defined rings followed by a very wide minimum and two more very faint maxima. The $s$ values averaged from six photographs and the estimated intensities are given in Table X. The six-term radial distribution function (Fig. 10) shows two peaks with maxima at 1.19 and 2.18 Å., the first corresponding to the N–O distance with the N–C distance unresolved and the second to the O–O and C–O distances.

TABLE X

NITROMETHANE

| Max. | Min. | $I$ | $s$ | $x$ | $\text{N–O}_{125°}$ |
|---|---|---|---|---|---|
| 1 | | 10 | 3.65 | 3.27 | (1.09 Å.) |
| | 2 | | 5.04 | 4.43 | (1.07) |
| 2 | | 30 | 6.50 | 6.26 | 1.175 |
| | 3 | | 7.96 | 8.00 | 1.226 |
| 3 | | 12 | 9.29 | 9.28 | 1.219 |
| | 4 | | 10.54 | 10.17 | 1.178 |
| 4 | | 12 | 11.75 | 11.83 | 1.228 |
| | 5 | | 13.47 | 13.61 | 1.231 |
| 5 | | 3 | 17.77 | 17.21 | 1.181 |
| | 6 | | 19.37 | 19.50 | 1.227 |
| 6 | | 2 | 21.02 | | |
| | | | | Average | 1.208 Å. |

Results: N–O = 1.21 ± 0.02 Å.
C–N = 1.46 ± 0.02 Å.
Angle O–N–O = 127 ± 3°

The photographs do not permit the evaluation of all the structural parameters. We expect, however, that the C–N distance has the single bond value 1.47 Å. and the N–O distances approximately the double bond value 1.22 Å. The three curves in Fig. 13 correspond to models having the relative dimensions determined by the above distances and the three values of the O–N–O angle, 120, 125 and 130°, respectively. The qualitative features of the photographs fix the angle at about 127°. Thus, the prominence of the third maximum relative to the fourth and the position and character of the fifth minimum as observed on the photograph eliminate the 120° model. In the 130° curve the position of the seventh maximum is a little better than in the one for 125° but the hump following the fifth minimum is too pronounced. The quantitative comparison (Table X) leads to the values C–N = 1.46 ± 0.02 Å. and N–O = 1.21 ± 0.02 Å., with the angle O–N–O = 127 ± 3°.

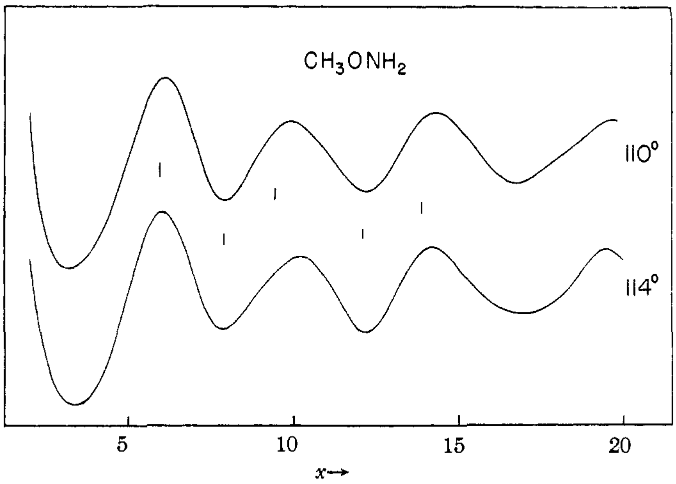

Fig. 12.—Intensity curves for $\alpha$-methylhydroxylamine.

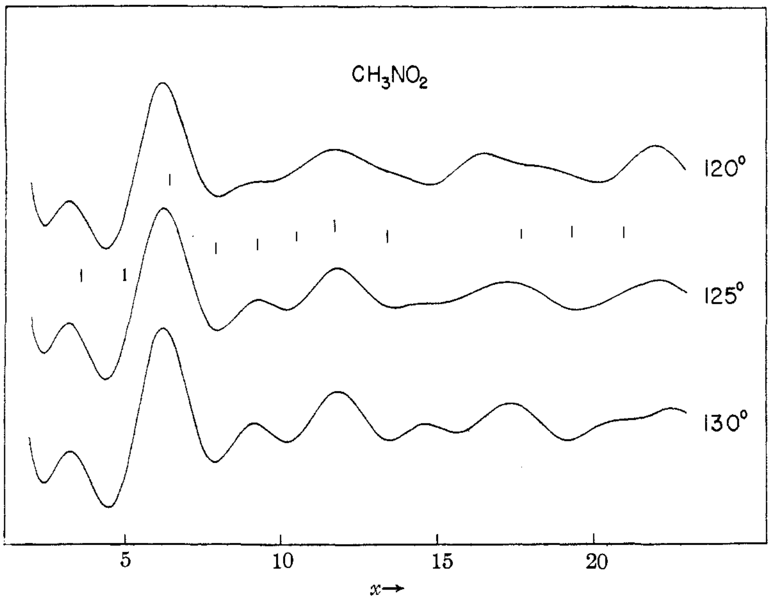

Fig. 13.—Intensity curves for nitromethane.

## Discussion of Results

In phosgene, thiophosgene and the six chloroethylenes the carbon–chlorine distances vary between 1.67 and 1.73 Å., being between 5 and 2% less than the normal single bond value 1.76 Å. This decrease is due to the partial double bond character caused by resonance resulting from the conjugation of an unshared pair of electrons on the chlorine atom with the adjacent double bond. The values found for the angle Cl–C–X are somewhat smaller than the tetrahedral value 125°16′ for the angle between a single bond and a double bond, as a result of the same phenomenon. A detailed discussion of these effects is given in the following paper.

For the other interatomic distances the values found are in good agreement with the table of covalent radii. In phosgene the carbon–oxygen distance has the double bond value 1.28 ± 0.02 Å. (1.28 Å. from the table), and for thiophosgene the double bond value 1.63 Å. for the carbon–sulfur distance leads to a satisfactory interpretation of the photographs. The N–O distance 1.21 ± 0.02 Å. for the nitro group in nitromethane is close to the double bond value 1.22 Å. The distances N–O = 1.37 ± 0.02 Å. and C–O = 1.44 ± 0.02 Å. in α-methylhydroxylamine and C–N = 1.46 ± 0.02 Å. in nitromethane agree well with the single bond values 1.36, 1.43 and 1.47 Å., respectively, given by the table of radii.

## Summary

The arrangements of atoms in molecules of phosgene, the six chloroethylenes, thiophosgene, α-methylhydroxylamine and nitromethane have been determined by the use of electron diffraction photographs, interpreted both by the radial distribution method and the usual visual method, with the following results. (Values given without attached probable errors were assumed to be correct in the investigation.)

Phosgene: C–Cl = 1.68 ± 0.02 Å.; C–O = 1.28 ± 0.02 Å.; angle Cl–C–O = 121.5 ± 1°.

| | C—C | C—Cl | Angle Cl—C—C |
|---|---|---|---|
| Vinyl chloride | 1.38 Å. | 1.69 ± 0.02 Å. | 122 ± 2° |
| 1,1-Dichloroethylene | 1.38 | 1.69 ± 0.02 | 122 ± 1° |
| *cis*-Dichloroethylene | 1.38 | 1.67 ± 0.03 | 123.5 ± 1° |
| *trans*-Dichloroethylene | 1.38 | 1.69 ± 0.02 | 122.5 ± 1° |
| Trichloroethylene | 1.38 | 1.71 ± 0.03 | 123 ± 2° |
| Tetrachloroethylene | 1.38 | 1.73 ± 0.02 | 123.75 ± 1° |

Thiophosgene: C–Cl = 1.70 ± 0.02 Å.; C–S = 1.63 Å.; angle Cl–C–S = 122°.
α-Methylhydroxylamine: N–O = 1.37 ± 0.02 Å.; O—C = 1.44 ± 0.02 Å.; angle C–O–N = 111 ± 3°.
Nitromethane: N–O = 1.21 ± 0.02 Å.; C–N = 1.46 ± 0.02 Å.; angle O–N–O = 127 ± 3°.

The discussion and interpretation of these results are given in the following paper.

Pasadena, California Received September 24, 1935