and Pt^{II} molecules of this type assume it. The salt of group 3 is explained in the same way. It thus resembles nickel dimethylglyoxime, which is also diamagnetic.

The diamagnetism of the salts of group 4 can be best explained by assuming a coupling between the spins of pairs of Pd^{II} ions. This coupling is of such a nature that it gives a zero resultant spin and also gives rise to the formation of a double molecule which can be observed in freezing point determinations. This explanation appears necessary for the salt listed in group 5. Otherwise the salt would be made up of single molecules with the Pd^{II} ion possessing an odd spin and therefore paramagnetism under all conditions.

Salts of the type of group 6 exist only in the case of Pt^{IV} and Pd^{IV}. The susceptibility is diamagnetic for the several Pt^{IV} salts that have been measured and for the two Pd^{IV} salts measured in this work. This can be explained in the same way as the diamagnetism of the salts of the group 2 type, that is, either by the breakdown of the Hund rule or by Pauling's theory of the electron pair bond. Here Pauling predicts that the salts of Pd^{IV} and Pt^{IV} are diamagnetic if the six possible electron pair bonds shared by groups in the molecule with the metallic ion extend to the corners of a regular tetrahedron.

The results show that the magnetic susceptibilities of Pd^{II} salts resemble closely those of Pt^{II}. In a few cases the susceptibilities of Ni^{II} salts resemble those of Pd^{II} and Pt^{II}. Only in the case of the dimethylglyoxime salt does Pd^{II} resemble Ni^{II}, exclusively. The corresponding Pt^{II} salt does not exist. The susceptibilities of Pd^{IV} salts closely resemble those of Pt^{IV}.

The author wishes to thank Professor J. H. Van Vleck for his continued interest in this work.

Summary

Using the Gouy method the magnetic susceptibilities of several typical palladium salts have been measured. In all cases the susceptibilities proved to be diamagnetic. An attempt is made to explain this behavior.

Madison, Wis. Received January 18, 1935

[Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 457]

The Electron Diffraction Investigation of the Molecular Structures of (1) Chlorine Monoxide, Oxygen Fluoride, Dimethyl Ether and 1,4-Dioxane and of (2) Methyl Chloride, Methylene Chloride and Chloroform, with Some Applications of the Results

By L. E. Sutton and L. O. Brockway

The electron diffraction method of investigating the structure of molecules has been sufficiently well developed that it now represents one of the most direct and practical means of obtaining information on bond distances and angles. The present communication gives the results of such investigations upon chlorine monoxide, oxygen fluoride, dimethyl ether and 1,4-dioxane, and the chlorinated methanes. These were made in order to test further the validity of the rule of additivity of atomic radii proposed by Sidgwick[1] and by Pauling,[2] to study the oxygen bond angle and to test the constancy of the carbon–chlorine bond angle. Some of the substances have been previously examined by other workers (as indicated below) but it seemed desirable to repeat their work.

Preparations

Chlorine Monoxide.—Chlorine monoxide was prepared by the method of Bodenstein and Kistiakowsky,[3] omitting the shaking of the reaction tube. Half of the product obtained was distilled off and rejected, in order to remove chlorine, while the remainder was distilled into a suitable container and used for the experiment. The sample was kept at −70° until just before it was used, when the temperature was raised to −40°. Photographs obtained from two separate preparations indicated that there was no appreciable decomposition of the chlorine monoxide.

Dimethyl Ether.—Dimethyl ether was prepared by the method of Krafft[4] and was stored and purified in solution in concentrated sulfuric acid.[5] From this it was regenerated by the addition of water, was dried and transferred to a suitable container at a pressure of 300 mm.

Oxygen Fluoride.—We are indebted to Professor Yost of this Laboratory for two samples of oxygen fluoride. They contained about four or five mole per cent. of oxygen,

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(1) N. V. Sidgwick, "Annual Reports of the Chemical Society," 1931; "The Covalent Link in Chemistry," Cornell University Press, 1933.

(2) Linus Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); Linus Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934).

(3) M. Bodenstein and G. B. Kistiakowsky, *Z. physik. Chem.*, **116**, 372 (1925).

(4) F. Krafft, *Ber.*, **26**, 2833 (1893).

(5) E. Erlenmeyer and A. Kriechbaumer, *ibid.*, **7**, 699 (1874).

the presence of which had no serious effect on the diffraction photographs.

1,4-Dioxane.—Commercial 1,4-dioxane was purified by the method of Herz and Lorentz,[6] a fraction of b. p. 99.9–100.6° being taken. The melting point, 10.37°, indicated that it was 98.8 mole per cent. pure,[7] which was sufficient for our purpose.

The bath temperature for the photographing was 50–65°.

Methyl Chloride.—Methyl chloride was prepared by the method of Norris and Taylor.[8] The gas was washed, dried, and passed through soda lime to remove hydrogen chloride. It was used at a pressure of 300 mm.

Methylene Chloride.—A commercial specimen was fractionated; the fraction used boiled at 39.5–40.1° (b. p. 40°, Landolt–Börnstein, 5th ed., 1923, Vol. I, p. 372). The bath temperature was 0°.

Chloroform.—C. P. chloroform was used, bath temperature −25°.

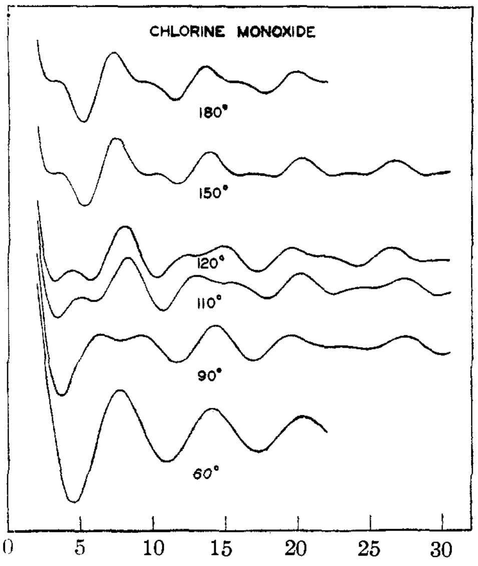

Fig. 1.—Simplified theoretical intensity curves for chlorine monoxide, in which the atomic scattering factor is set equal to the atomic number.

Electron Diffraction Photographs.—The technique used in obtaining electron diffraction photographs has been discussed.[9] The effective wave lengths of the electron beam corresponding to given readings of the primary voltmeter were obtained by calibrations with photographs of gold leaf; they were approximately 0.06 Å. The distance from the point of diffraction to the photographic film was 12.19 cm. The photographs obtained were interpreted by the visual method, first used by Wierl,[10] which has been critically examined by Pauling and Brockway,[9] who conclude that if it is applied carefully it can give interatomic distances accurate to about 1%. In measuring the diameter of the visual maxima and minima three readings were taken for each on the best photographs and two or even only one on the medium quality photographs so that the simple average of all these results was a roughly weighted mean. In order to eliminate personal error as far as possible, readings were made independently by two observers, and the mean of all the readings was used for the calculation of distances.

The exact treatment given each substance will be described under the particular headings, but it may be explained that since all the triatomic or pseudotriatomic molecules (*i. e.*, those having three main scattering atoms) which were examined were of the type $\overset{\mathrm{X}}{\mathrm{Y}\diagup\;\diagdown\mathrm{Y}}$, and therefore had the atoms at the apices of an isosceles triangle; they could all be characterized by the values of two parameters. We chose as these the bond distance $l_{\mathrm{X-Y}}$ and the angle beween the two X–Y bonds, $\Theta_{\mathrm{Y-X-Y}}$; the distance $l_{\mathrm{Y-Y}}$ was then derived from the observed values of these parameters. In no case could the distances between hydrogen and other atoms be directly determined, but in several compounds it was necessary to include the intensity of the diffraction between such pairs, and in order to do this $l_{\mathrm{C-H}}$ was assumed[2] to be 1.06 Å., and the tetrahedral angle (109°28′) was assumed between the carbon–hydrogen bonds.

Chlorine Monoxide.—The qualitative description of the photographs was the following: a weak first maximum, a weak second minimum, a strong broad second maximum, a strong third minimum, a medium strong third maximum followed by a broad shelf or possibly by a very weak fourth minimum and fourth maximum, a strong broad fifth minimum, and a fairly strong narrow fifth maximum. The first three maxima were approximately equally spaced; the next definite maximum (the fifth) was separated by a wide interval from the third.

Comparison of the photographs with the curves shown in Fig. 1 showed that they corresponded most closely to the curve for $\Theta_{\mathrm{Cl-O-Cl}} = 110°$, as may easily be verified by comparing the above description with the curves. A more detailed comparison with the series of curves over a narrower range of Θ, 105–115°, shown in Fig. 2, showed that Θ must be less than 115°, because

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[6] W. Herz and E. Lorentz, *Z. physik. Chem.*, **A140**, 406 (1929).

[7] W. A. Roth and I. Meyer, *Z. Elektrochem.*, **39**, 35 (1933).

[8] J. F. Norris and H. B. Taylor, This Journal, **46**, 753 (1924).

[9] Linus Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934). A detailed description of the apparatus will be published soon.

[10] R. Wierl, *Ann. Physik*, [5] **8**, 521 (1931).

the fourth maximum is weaker than the third, but more than 105°, because this appears to be a maximum rather than merely a shelf. On the photographs a very faint seventh maximum was observed (which was identified by approximate measurements on the diameter) whereas the sixth maximum did not appear at all. This fact definitely eliminates the 105° model. The most probable range for $\Theta_{\mathrm{Cl-O-Cl}}$ is considered to be 108–113°, and the most probable value is 111°.

The values of $(4\pi \sin \Theta/2)/\lambda$ calculated from the observed diameters of the different maxima and minima, and the corresponding values of $l_{\mathrm{O-Cl}}$, calculated for $\Theta_{\mathrm{Cl-O-Cl}} = 105, 108, 110, 112,$ and 115°, are given in Table I. These results are from the photographs taken with the second batch of chlorine monoxide, which were considerably cleaner and sharper than those taken with the first batch; the mean values of $l_{\mathrm{O-Cl}}$ from each lot agree to within less than 0.01 Å., however, showing that they are essentially the same.

TABLE I

CHLORINE MONOXIDE

Nine photographs Wave length = 0.0606 Å.

Max.	Min.	$\frac{4\pi \sin \Theta/2}{\lambda}$	x 105°	x 108°	x 110°	x 112°	x 115°	$l_{\mathrm{O-Cl}}$ 105°	$l_{\mathrm{O-Cl}}$ 108°	$l_{\mathrm{O-Cl}}$ 110°	$l_{\mathrm{O-Cl}}$ 112°	$l_{\mathrm{O-Cl}}$ 115°
1		2.801	5.35	5.20	4.98	4.90	4.67	(1.910)	(1.855)	(1.778)	(1.749)	(1.665)
	2	3.800		6.00	6.00	5.90	5.80		(1.579)	(1.579)	(1.553)	(1.525)
2		4.835	8.45	8.35	8.25	8.20	8.10	1.748	1.727	1.706	1.696	1.675
	3	6.298	10.90	10.75	10.65	10.60	10.55	1.731	1.708	1.692	1.684	1.675
3		7.328	13.25	13.10	12.95	13.00	12.80	(1.808)	(1.789)	(1.767)	(1.774)	(1.747)
	4	8.364				14.30	13.75				(1.710)	(1.645)
4		9.143				15.50	15.20				(1.695)	(1.663)
	5	10.40	18.25	18.00	17.85	17.70	17.60	1.756	1.732	1.717	1.702	1.693
5		11.45	20.60	20.30	20.20	20.05	19.80	1.785	1.759	1.750	1.737	1.715
						Weighted means		1.755	1.73	1.72	1.705	1.69

Final value: $l_{\mathrm{Cl-O}} = 1.71 \pm 0.02$ Å. $\Theta_{\mathrm{Cl-O-Cl}} = 111 \pm 2°$.

The values of x are those for which there are maxima or minima on the theoretical intensity curve.

The weighted mean values were derived by rejecting the values found from the first, third, and fourth maxima, and the second and fourth minima, and taking the arithmetic mean of the remaining four values. This was done because previous experience[9,11,12] had shown that measurements of the first maximum and second minimum when they are of the order of 1 cm. in diameter are affected by contrast effects of the dense central image and because, as they are notably unsymmetric, readings of them should be subject to the St. John effect[9] and so give a high and a low value, respectively, as they actually do. The third maximum is also subject to this latter effect and consequently gives too high a value. Values from the fourth minimum and fourth maximum were rejected because for angles of 105–110° they were so indefinite on the theoretical curves that they could not be expected to give reliable results; for the angle 112° they do give concordant results, although this is probably accidental, and if included make no appreciable difference to the mean value.

The estimated probable error is a little more than 1% due to uncertainty in the voltage at the instant of exposure and to other errors inherent in the method of interpreting the photographs. The final result is $\Theta = 111 \pm 2°$, $l_{\mathrm{O-Cl}} = 1.71 \pm 0.02$ Å. and $l_{\mathrm{Cl-Cl}} = 2.82 \pm 0.03$ Å.

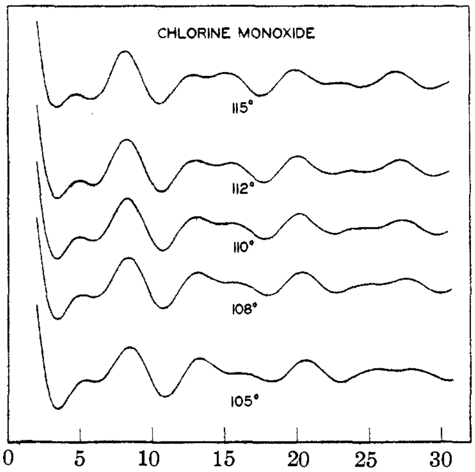

Fig. 2.—Theoretical intensity curves for chlorine monoxide covering a narrower range of the bond angle.

Oxygen Fluoride.—The photographs showed a broad, almost uniform shelf spreading out from

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(11) V. E. Cosslett and H. G. de Laszlo, *Nature*, **134**, 63 (1934).

(12) V. E. Cosslett, *Trans. Faraday Soc.*, **30**, 981 (1934).

the central image, with a faint maximum near the edge, followed by a fairly strong minimum and then a fairly strong, quite well-defined maximum. Comparison with the theoretical intensity curves shown in Fig. 3 indicates that the angle Θ_{F-O-F} cannot be more than 110° and is probably less, on account of the sharpness of the second maximum; a probable value is therefore 105 ± 5°.

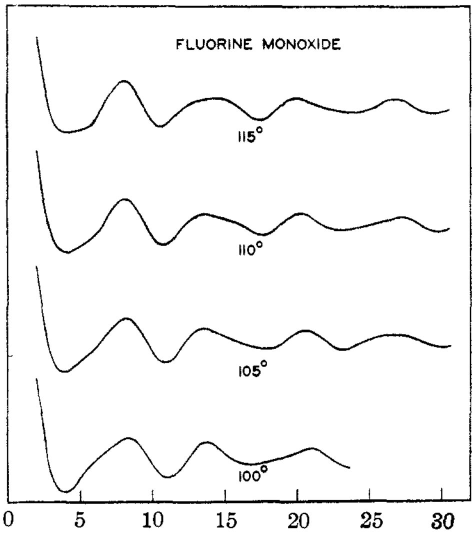

Fig. 3.—Theoretical intensity curves for oxygen fluoride.

In Table II the value from the second maximum is not included in deriving the mean value because of the pronounced asymmetry of this ring. The diameter of the first maximum is large enough so that its measurement is not as greatly affected as in the heavier molecules. The pictures are not exceptionally clean because of the difficulty of condensing the oxygen fluoride; accordingly a large probable error is expected. The final values are Θ_{F-O-F} = 105 ± 5° and l_{O-F} = 1.36 ± 0.10 Å. We hope that subsequent investigations may be carried out which will fix the size of the molecule within a narrower range.

Table II

Oxygen Fluoride

Ten photographs

λ = 0.0606 Å.

Max.	Min.	$\frac{4\pi \sin \Theta/2}{\lambda}$	x 100°	105°	110°	115°	l_{O-F} 100°	105°	110°	115°
1		6.10	8.35	8.20	8.12	8.06	1.37	1.34	1.33	1.32
	2	7.73	11.0	10.90	10.70	10.55	1.42	1.41	1.385	1.365
2		9.13	13.75	13.60	13.50	14.70	(1.50)	(1.49)	(1.48)	(1.61)
						Average	1.40	1.38	1.36	1.34

Final value l_{O-F} = 1.36 ± 0.10 Å.

l_{F-F} = 2.16 ± 0.20 Å.

Θ_{F-O-F} = 105 ± 5°

Dimethyl Ether.—The calculation of the theoretical scattering for dimethyl ether is complicated by the possibility of rotation of each methyl group around the corresponding carbon–oxygen bond. The number of carbon–hydrogen terms is too great to be neglected, but the distances between the carbon atom of one methyl group and the hydrogen atoms of the other varies with the orientation of the methyl groups. An approximate treatment was given by the method of Wierl[13] in which the rotating group is considered in a set of definite positions corresponding to regular intervals of the rotation angle. The contribution to the scattering which is made by the variable terms is calculated for each definite position, and an average effect is determined in which the individual weights depend on the nature of the rotation. In this case the calculations are simplified by the equivalence of the two rotating groups and by the trigonal symmetry axis of each group. Intervals of 30° in the rotation angle (starting with a C–H bond in the C–O–C plane) were used and with the assumption of unrestricted rotation

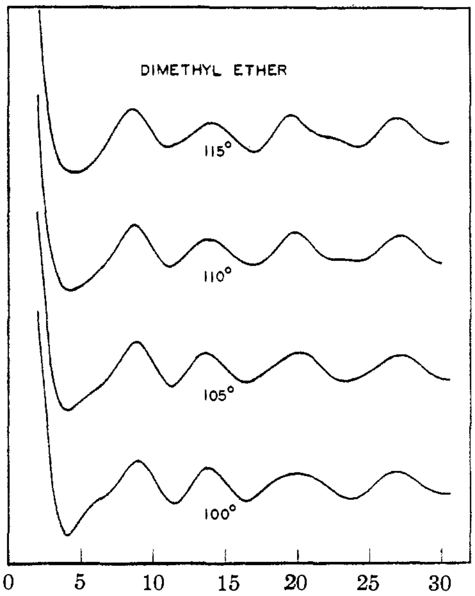

Fig. 4.—Theoretical intensity curves for dimethyl ether. An allowance has been made for free rotation of the methyl groups.

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(13) R. Wierl, *Ann. Physik*, [5] **13**, 453 (1932).

equal weights were given to the various positions. This treatment was entirely adequate since the addition of these terms to the curve calculated without them made only very slight changes in the positions of the maxima and minima.

Table III gives the values of the carbon–oxygen bond length calculated for models with Θ_{C-O-C} equal to 100, 105, 110 and 115°.

The photographs show a quite regular series of rings with an especially wide minimum between the third and fourth maxima. This fixes the angle near 110° and the most probable value is chosen as 111 ± 4° while the bond distance, l_{C-O}, is 1.44 ± 0.03 Å.

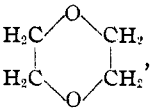
TABLE III

DIMETHYL ETHER

		Six photographs	x				$\lambda = 0.0606$ Å. l_{C-O}			
Max.	Min.	$\frac{4\pi \sin \Theta/2}{\lambda}$	100°	105°	110°	115°	100°	105°	110°	115°
1		6.024	8.85	8.85	8.75	8.55	1.470	1.470	1.453	1.420
	2	8.193	11.38	11.25	11.15	11.05	1.390	1.374	1.361	1.349
2		9.744	13.80	13.70	13.80	14.20	1.416	1.405	1.416	1.457
	3	12.12	16.40	16.30	16.90	16.95	1.353	1.345	1.395	1.398
3		13.63	19.80	20.25	19.85	19.65	1.452	1.485	1.455	1.441
	4	16.00	23.70	23.20		24.25	1.481	1.450		1.515
4		17.78	26.80	27.25	27.10	26.95	1.507	1.532	1.524	1.515
					Average		1.438	1.437	1.434	1.442
					Average deviation		0.045	0.054	0.043	0.046

Final value $l_{C-O} = 1.44 \pm 0.03$ Å.
$l_{C-C} = 2.39 \pm 0.05$ Å. $\Theta_{C-O-C} = 111 \pm 4°$

1,4 - Dioxane.—The 1,4-dioxane molecule,



may have one of two configurations, the "chair" or Z-form and the "cradle" or C-form. Each of these can be specified by four parameters, the bond distances and the angles l_{C-O}, l_{C-C}, Θ_{C-O-C} and Θ_{C-C-O}. The simultaneous evaluation of these parameters would require photographs of extremely good quality and involve very extensive labor. The photographs were only fair in quality so a complete treatment was not attempted. We assumed the value 1.54 Å. for l_{C-C}, 1.06 Å. for l_{C-H}, 109°28′ for all of the carbon bond angles, and then calculated curves for the Z- and C- forms with l_{C-O} equal to 1.44 Å. and Θ_{C-O-C} equal to 110°. Only the hydrogen–hydrogen diffraction terms were neglected.

The photographs show a narrow, sharp first maximum, a broad heavy second maximum, a well-defined third maximum followed by a deep fourth minimum and a weak fourth maximum. The 110° curves in Fig. 5 show that the substance must be mainly in the Z-form, because the double third maximum eliminates the curves for the C-form.

Additional curves for the Z-form, with Θ_{C-O-C} equal to 105 and 115° and the other parameters unaltered, were calculated but the changes in angle had scarcely any effect on the positions of the important maxima and minima. The curve for 110° looks rather more like the photographs but the other two models cannot be definitely excluded. The value $\Theta_{C-O-C} = 110 \pm 5°$ is accurate within the indicated probable error.

Table IV shows the calculated values of l_{C-O}. The mean value, 1.46 Å., is somewhat larger than the one initially assumed; but since further treatment is impossible at this time we quote the

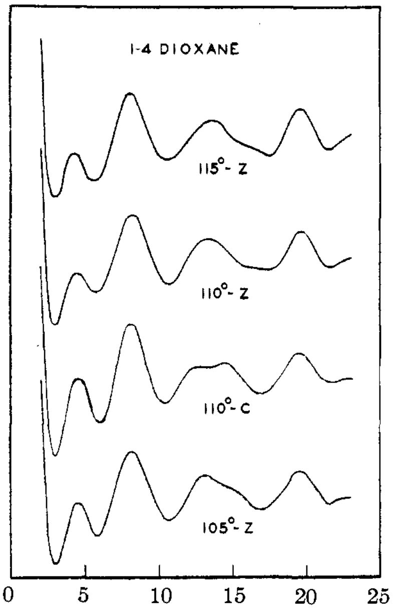


Fig. 5.—Theoretical intensity curves for dioxane. The C–O–C bond angle is varied in these curves.

TABLE IV

1,4-DIOXANE, Z CONFIGURATION

Six photographs $\lambda = 0.0606$ Å.

Max.	Min.	$\frac{4\pi \sin \theta/2}{\lambda}$	x 105°	x 110°	x 115°	l_{C-O} 105°	l_{C-O} 110°	l_{C-O} 115°
1		3.16	4.55	4.50	4.25	(1.445)	(1.429)	(1.350)
	2	4.31	5.85	5.80	5.60	(1.357)	(1.345)	(1.299)
2		5.55	8.20	8.20	8.10	1.477	1.477	1.460
	3	7.57	10.70	10.70	10.56	1.414	1.414	1.395
3		9.10	13.15	13.34	13.60	1.445	1.465	1.495
	4	11.73	17.40	17.60	17.50	(1.483)	(1.500)	(1.491)
4		13.29	19.60	19.70	19.60	1.475	1.482	1.475
					Average	1.452	1.459	1.456
					Average deviation	0.026	0.023	0.031

Final value, $l_{C-O} = 1.46 \pm 0.04$ Å.
$\theta_{C-O-C} = 110 \pm 5°$.

result with an error larger than usual, $l_{C-O} = 1.46 \pm 0.04$ Å.

Methyl Chloride.—The four bonds were assumed to be directed along the axes of a regular tetrahedron, and l_{C-H} was taken as 1.06 Å. The curve is shown in Fig. 6.

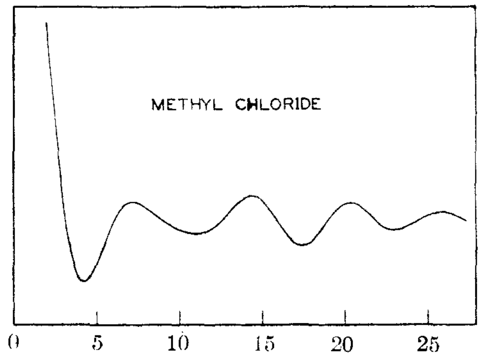


Fig. 6.—Theoretical intensity curve for methyl chloride.

The photographs showed a fairly strong first minimum, a fairly strong but broad and ill-defined first maximum, a weak second minimum, a medium strong and well-defined second maximum, a strong third minimum, and a fairly strong, sharp third maximum. Some photographs showed a weak fourth minimum and weak fourth maximum.

TABLE V

METHYL CHLORIDE

Four photographs $\lambda = 0.0606$ Å.

Max.	Min.	$\frac{4\pi \sin \theta/2}{\lambda}$	x	l_{C-Cl}
1		4.068	7.20	1.770
	2	6.317	10.93	1.733
2		8.119	14.40	1.774
	3	9.845	17.45	1.772
3		11.24	20.40	1.815
	4	13.08	23.15	1.769
4		14.49	25.80	1.781
			Average	1.773
			Average deviation	0.013

Final value, $l_{C-Cl} = 1.77 \pm 0.02$ Å.

The interval between the first and second maxima was greater than that between the other maxima, which were approximately equally spaced. The l_{C-Cl} values obtained are given in Table V.

Methylene Chloride.—The photographs may be described as follows: a weak first maximum, a weak second minimum, a strong second maximum, a strong third minimum, a distinctly double maximum (third and fourth maxima) of medium strength with a weak minimum between the peaks, the third maximum being somewhat stronger than the fourth, a medium strong fifth minimum and a weak but well-defined fifth maximum. One photograph showed two further, very faint maxima. The maxima were approximately equally spaced. Comparison with Fig. 7 shows that a conservative upper limit of 115° for the bond angle (Cl–C–Cl) is fixed by the relative appearance of the fourth and third maxima; that the seventh is considerably stronger than the sixth maximum requires the angle to be greater than 108°.

Table VI gives the quantitative results. It is to be noted that the percentage variation in the Cl–Cl distance with change in bond angle is less than that in the C–Cl distance. The greater atomic number of the chlorine atoms makes the Cl–Cl interference effects more important than those due to C–Cl pairs. The final values are $\theta_{Cl-C-Cl} = 111 \pm 2°$, $l_{C-Cl} = 1.77 \pm 0.03$ Å. and $l_{Cl-Cl} = 2.92 \pm 0.02$ Å.

Chloroform.—The molecule was assumed to have an axis of three-fold symmetry about the carbon-hydrogen bond.

The qualitative description of the photographs was the following: a strong first maximum, a strong second minimum, a very strong second maximum, a very strong third minimum, a medium strong fourth maximum, a medium strong fifth minimum, a medium strong fifth maximum,

TABLE VI

METHYLENE CHLORIDE

Max.	Min.	Photos	$\frac{4\pi \sin \Theta/2}{\lambda}$	x 108°	110°	112°	115°	l_{C-Cl} 108°	110°	112°	115°
1		7	2.809	5.15	5.05	5.00	4.85	(1.834)	(1.798)	(1.780)	(1.726)
	2	7	3.788	6.42	6.30	6.22	6.10	(1.695)	(1.663)	(1.644)	(1.610)
2		9	4.805	8.42	8.37	8.27	8.10	1.753	1.742	1.721	1.685
	3	9	6.069	10.70	10.55	10.52	10.40	1.762	1.738	1.733	1.713
3		9	6.998	13.02	12.95	12.65	12.45	1.860	1.850	1.808	1.780
	4										
4		8	8.842	15.82	15.68	15.50	15.35	1.790	1.773	1.753	1.736
	5	8	9.99	18.01	17.90	17.77	17.60	1.803	1.792	1.779	1.762
5		9	11.01	20.33	20.18	20.05	19.86	1.846	1.832	1.820	1.804
	6	2	12.47	22.60	22.45	22.25	21.90	1.812	1.800	1.785	1.756
6		2	13.28	24.65	24.37	24.00	22.95	1.855	1.833	1.806	1.727
	7	2	14.45	26.13	25.65	25.20	24.60	1.809	1.775	1.744	1.703
7		2	15.41	27.85	27.52	27.20	26.85	1.806	1.786	1.765	1.742
	8										
8		1	17.94	32.13	31.78	31.40	31.0	1.792	1.771	1.751	1.728
Final value, $l_{C-Cl} = 1.77 \pm 0.03$.						Weighted average		1.793	1.777	1.762	1.739
$\Theta_{Cl-C-Cl} = 111 \pm 2°$.						Average deviation		0.027	0.028	0.030	0.033
$l_{Cl-Cl} = 2.92 \pm 0.02$.						l_{Cl-Cl}		2.902	2.912	2.921	2.932

less strong than the fourth, a strong sixth minimum, a strong sixth maximum, a strong seventh minimum, a weak seventh maximum, a weak eighth minimum, a weak eighth maximum, rather stronger than the seventh, and on some photographs a very weak ninth minimum and a very weak ninth maximum. The maxima were all approximately equally spaced.

The theoretical curves in Fig. 8 show that the bond angle is less than 115° since the fourth maximum is weaker than both the third and the fifth; seven stronger than both six and eight requires the angle to be larger than 107°. Table VII indicates that the calculated Cl–Cl distance is quite independent of the assumed angle; the principal scattering occurs at the chlorine atoms. The results are $\Theta_{Cl-C-Cl} = 111 \pm 2°$, $l_{C-Cl} = 1.78 \pm 0.03$ Å. and $l_{Cl-Cl} = 2.93 \pm 0.02$ Å.

Discussion

The results of the measurements on the oxygen compounds are given in Table VIII which includes two previous results. We believe that the earlier values quoted by Brú are less reliable than the results of the present work.

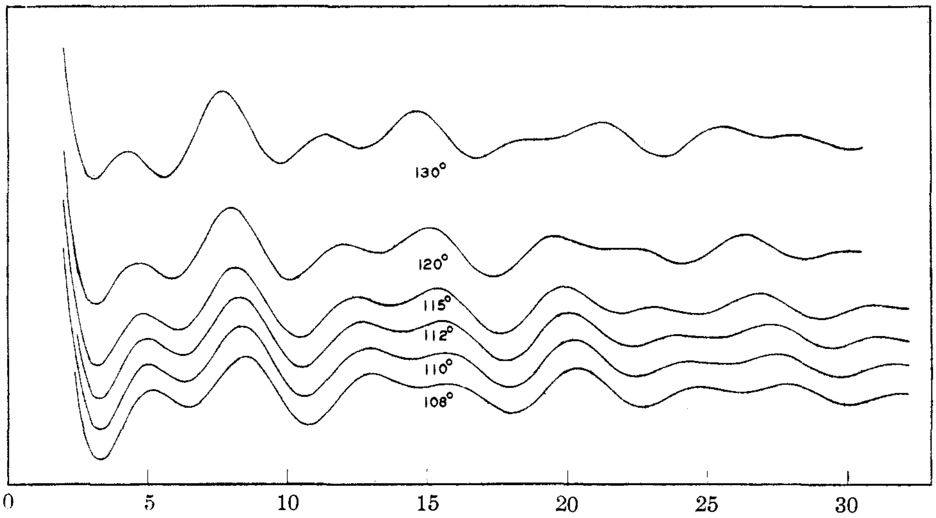


Fig. 7.—Theoretical intensity curves for methylene chloride.

The observed length of the oxygen–chlorine bond in chlorine monoxide is greater than that predicted from the Pauling–Huggins[2] table of atomic radii, 1.65 Å. ($r_O = 0.66$ Å. and $r_{Cl} = 0.99$ Å.). While it is possible that the difference

TABLE VII

CHLOROFORM

			Five photographs		x		λ = 0.0606 Å.	l_{C-Cl}		
Max.	Min.	$\frac{4\pi\sin\theta/2}{\lambda}$	107°	110°	112°	115°	107°	110°	112°	115°
1		2.744	4.90	4.85	4.75	4.65	(1.785)	(1.766)	(1.730)	(1.694)
	2	3.752	6.62	6.45	6.40	6.26	(1.764)	(1.718)	(1.705)	(1.668)
2		4.776	8.60	8.42	8.35	8.20	1.801	1.763	1.748	1.716
	3	6.042	10.80	10.60	10.45	10.35	1.786	1.754	1.729	1.713
3		6.992	12.88	12.60	12.50	12.30	1.842	1.802	1.788	1.760
	4	8.083	14.75	14.40	14.15	13.92	1.825	1.781	1.751	1.723
4		9.037	16.38	16.08	15.85	15.65	1.813	1.780	1.755	1.732
	5	10.20	18.17	18.08	17.85	17.55	1.781	1.774	1.750	1.721
5		11.16	20.45	20.13	20.00	19.62	1.831	1.803	1.791	1.756
	6	12.43	22.60	22.30	22.05	21.68	1.820	1.795	1.775	1.745
6		13.32	24.60	24.10	23.75	23.20	1.846	1.809	1.783	1.741
	7	14.55	26.35	25.72	25.40	24.85	1.811	1.769	1.746	1.708
7		15.32	28.13	27.63	27.30	27.00	1.836	1.804	1.782	1.762
	8	16.57	30.22	29.74	29.45	28.95	1.824	1.795	1.777	1.747
8		17.47	32.37	31.73	31.45	30.90	1.853	1.816	1.801	1.769
Final value, l_{C-Cl} = 1.78 ± 0.03 Å					Averages		1.821	1.787	1.767	1.738
l_{Cl-Cl} = 2.93 ± 0.02 Å.					Average deviation		0.018	0.016	0.019	0.017
$\theta_{Cl-C-Cl}$ = 111 ± 2°.					l_{Cl-Cl}		2.929	2.930	2.931	2.931

TABLE VIII

Compound	l_{X-X}, Å.	θ_{X-O-X}	l_{O-X}, Å.	
Chlorine monoxide	2.82 ± 0.02	111 ± 2°	1.71 ± 0.02	
Oxygen fluoride	2.2 ± .2	105 ± 5°	1.4 ± .1	
Dimethyl ether	2.38 ± .05	111 ± 4°	1.44 ± .03	
	2.05 ± .10	100°	1.34 ± .06	Brú[14]
Diethyl ether	2.04 ± .14	100°	1.33 ± .08	Brú[14]
1,4-Dioxane	2.39 ± .10	110 ± 5°	1.46 ± .04	

is due to experimental error, it is certainly beyond the limit of probable error. The observed carbon–oxygen distances, on the other hand, agree well with the sum of the radii, 1.43 Å. (r_C = 0.77 Å.). The sum of the oxygen–fluorine radii is 1.30 Å. (r_F = 0.64 Å.), and while the large probable error in the observed distance allows rough agreement with the predicted value, no useful comparisons can be made with the present data.

The direction of the chlorine–oxygen discrepancy makes it difficult to find any reasonable explanation. Brockway and Wall[15] found discrepancies between the predicted and observed bond lengths in the halides of silicon, tin and elements of Group V, but the observed values were always less than the predicted, and an explanation was suggested based on the polar character of the bonds between unlike atoms as compared with those between like atoms from which the radii in the table were derived. It is possible that the oxygen radius in a non-polar bond should be 0.72 Å.[16] or larger in order that its sum with the chlorine radius, 0.99 Å., taken from chlorine molecule, should agree with the observed distance, and the shortening of 0.05 Å. which this would introduce in the carbon–oxygen bond would be attributed to the polar character of this bond. This purely tentative suggestion emphasizes the need for direct study of the oxygen nonpolar bond radius in such a compound as hydrogen peroxide. It is evident that the rule of additivity of atomic radii is only approximate.

The oxygen bond angle in chlorine monoxide is 111 ± 2°, in dimethyl ether it is 111 ± 4°, and in 1,4-dioxane it is 110 ± 5°, in oxygen fluoride, on the other hand, it is certainly less than 110°, being probably 105 ± 5°. In the last compound it has about the same value as the oxygen bond angle in water, 105°6′.[17] Its greater value in the other compounds is presumably due to the repulsion

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[14] L. Brú, *Anales soc. españ. fís. quím.*, **30**, 486 (1932).

[15] L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934).

[16] The value of the oxygen radius given by Sidgwick[1] is 0.70 Å., but this was derived with the aid of a value for the carbon–carbon double bond which is probably too small [R. Badger, *Phys. Rev.*, **45**, 648 (1934) gives 1.37 Å. from ethylene] and on the assumption that the bond in the normal oxygen molecule is a true double bond, which cannot be so because of the magnetic properties of the molecule.

[17] R. Mecke, *Z. Physik*, **81**, 313 (1933); R. Mecke and W. Baumann, *ibid.*, **81**, 445 (1933).

between the comparatively large chlorine atoms or methyl groups. $l_{\text{Cl-Cl}}$ in chlorine monoxide is 2.82 ± 0.03 Å. In methylene chloride $\Theta_{\text{Cl-C-Cl}}$ is 111 ± 2° and $l_{\text{Cl-Cl}}$ is 2.92 ± 0.02 Å. Each of these chlorine–chlorine distances is less than the normal closest approach of two non-bonded atoms, for Dickinson and Bilicke[18] found that the least distance between two chlorine atoms belonging to two different molecules of crystalline benzene hexachloride is 3.74 Å., and Huggins[19] reports that in other crystals the effective non-bonded radius of a chlorine atom is about 1.85 Å. It is evident that the repulsive forces between the chlorine atoms are abnormally great since they have been brought close together by the attractive forces which bond them to a third atom; this "steric repulsion" is greater in the case of chlorine monoxide than for methylene chloride, as would be expected from the earlier prediction[20] that the bond angle for oxygen when the repulsive forces between the atoms bonded to it are negligible is less than the corresponding "natural" angle for carbon. The distance between the carbon atoms in dimethyl ether, 2.38 Å., is also considerably less than the minimum distance of 3.4–3.9 Å., which Hendricks[21] has found to exist between carbon atoms which are not linked to one another. The enlargement of angle in this compound, too, can be accounted for by the abnormal repulsive forces between the non-bonded atoms. If the effective radii of the hydrogen atoms on the methyl groups be taken as the sum of their covalent radii and an envelope 0.5 Å. thick,[22] they will not interfere with each other even in their positions of closest approach, and there should be little hindrance of the freedom of rotation of these groups from this cause.

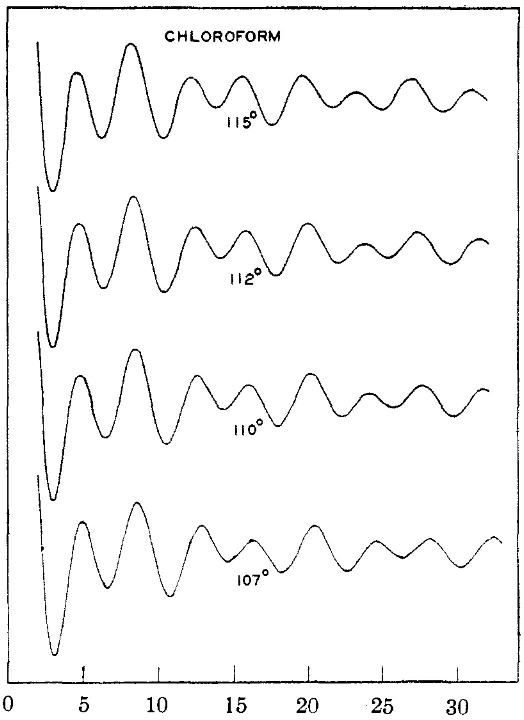

Fig. 8.—Theoretical intensity curves for chloroform.

TABLE IX

Compound	$l_{\text{Cl-Cl}}$, Å.	$\Theta_{\text{Cl-C-Cl}}$	$l_{\text{C-Cl}}$, Å.	
Methyl chloride			1.77 ± 0.02	
			1.85 ± .06	Electron[23]
			1.80 ± .1	x-Ray[24]
Methylene chloride	2.92 ± 0.02	111 ± 2°	1.77 ± .03	
	3.16 ± .06	110 to 115°	1.86 ± .04	Electron[10]
	3.23 ± .1	124 ± 6°	(1.83)	x-Ray[24]
Chloroform	2.93 ± .02	111 ± 2°	1.78 ± .03	
	3.04 ± .04			Electron[10]
	3.11 ± .05	116 ± 3°	(1.83)	x-Ray[24]
Carbon tetrachloride	2.87 ± .01	(109° 28′)	1.760 ± .005	
	2.98 ± .03	(109° 28′)	1.82 ± .02	Electron[10]
	2.99 ± .03	(109° 28′)	1.83 ± .02	x-Ray[24]

The results for the chlorinated methanes (including carbon tetrachloride) are given in Table IX together with the results of other investigators who have worked on the same set of compounds.

Our results support Wierl's conclusion that the carbon–chlorine bond distance is practically constant in this series. The discrepancy in absolute value has been discussed at length by Pauling and Brockway.[9] Their lower value for the size of the carbon tetrachloride molecule is supported by the

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(18) R. G. Dickinson and Bilicke, THIS JOURNAL, **50**, 764 (1928).

(19) M. L. Huggins, *Chem. Rev.*, **10**, 447 (1932).

(20) Linus Pauling, THIS JOURNAL, **53**, 1367 (1931).

(21) S. B. Hendricks, *Chem. Rev.*, **7**, 431 (1930).

(22) N. V. Sidgwick, "Annual Reports of the Chemical Society," **29**, 70 (1932).

(23) R. Wierl, Reference 10, note on page 564.

(24) L. Bewilogua, *Physik. Z.*, **32**, 265 (1931).

results of other recent investigations.[11,12] The sum of the covalent radii is 1.76 Å., a value which lies within the range of the probable experimental error for each of the observed distances. It may be pointed out that the polar character of the carbon–chlorine bond is not strong enough to produce the shortening observed in the molecules of the chlorides of silicon, tin, phosphorus, and arsenic.[15]

The angle between the carbon–chlorine bonds is found to be remarkably constant in these compounds, the probable increase above the tetrahedral angle being only 2° in the case of chloroform and methylene chloride. Bewilogua using x-ray diffraction methods could not make a direct determination of the angles because of the low scattering power for x-rays of carbon relative to chlorine. He assumed constancy of the carbon–chlorine bond distance and with the aid of the value which he found for it in carbon tetrachloride he calculated the angles in other compounds from the observed chlorine–chlorine distances. The validity of this assumption is demonstrated above. The discrepancy between the x-ray and electron diffraction results is probably due to an inherent difference in the accuracy of the two methods as a means of determining molecular size.[9]

The table shows an increase in the chlorine–chlorine distance from 2.87 Å. in carbon tetrachloride to 2.93 and 2.92 Å. in chloroform and methylene chloride. Because of the lesser accuracy of the determination of the carbon–chlorine distances we cannot say with any certainty whether the increase in the chlorine atom separations is accompanied by an increase in angle or an increase in carbon–chlorine distance or both. A simple theoretical calculation may be made of the effect of the repulsive forces between the chlorine atoms on the bending and stretching of the carbon–chlorine bonds. If the ratio between the radial and the bending force constants of the bond[25] is about 5, it is found that there should be an increase in the bond distance in going from methylene chloride to carbon tetrachloride of from 0.02 to 0.05 Å. depending on the method used in evaluating the repulsive forces. Since the observed bond distances show that such an increase lies outside the range of experimental error but that a small decrease is possible, it is evident either that the repulsive forces between the chlorine atoms are less effective in stretching the bonds than we have assumed, or that there is some compensating effect tending to make the C–Cl distance shorter as more chlorine atoms are introduced into the molecule, such as some kind of mutual interaction of the bonds. We believe that the carbon–chlorine bond distance in the chlorinated methanes is substantially constant and that the bond angle is increased by 2 or 3° above the tetrahedral value in chloroform and methylene chloride.

Application of Electron Diffraction Data to the Discussion of Electric Moment Data.—The evidence of the electron diffraction photographs of 1,4-dioxane that this substance exists in the chair or Z-form rather than the cradle or C-form is in agreement with the electric dipole moment evidence. Earlier values for the moment were approximately 0.4 *D*, which would indicate that the molar percentage of the C-form is only 2–5%, but the latest value, zero,[26] shows that the substance exists wholly in the Z-form.

Using electron diffraction data in conjunction with electric dipole moment data, it is now possible to calculate in a fairly satisfactory manner the effect of the moment of one bond upon that of the other. To do so it is necessary to make some assumption about the relative magnitude of the moments of the carbon–hydrogen and carbon–chlorine bonds (or groups), and the simplest one is that the former is very small relative to the latter.[27] Then, since $\mu_{\mathrm{CH_2Cl_2}} = 2\mu_{\mathrm{C-Cl}} \cos \Theta_{\mathrm{Cl-C-Cl}}/2$, $\mu_{\mathrm{CHCl_3}} = \mu_{\mathrm{C-Cl}} \sqrt{(6 \cos \Theta_{\mathrm{Cl-C-Cl}} + 3)}$, $\mu_{\mathrm{CH_2Cl_2}} = 1.55\ D$, and $\mu_{\mathrm{CHCl_3}} = 1.0\ D$, it follows that $\mu_{\mathrm{C-Cl}}$ is approximately 1.35 *D* in methylene chloride and 1.28 *D* in chloroform, whereas it is approximately 1.85 *D* in methyl chloride. The mutual effect of the dipoles therefore reduces the moment by 30%. This is a minimum estimate, for if the moments of the carbon–hydrogen bonds were not negligible, then since their resultant must be in the same direction as that of the carbon–chlorine bonds, and since their polarizability is less, the proportional changes calculated in the latter bonds would be still greater.

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[25] The radial force constant for the carbon chlorine bond is 3.1 × 10^6 dynes per cm. [K. W. F. Kohlrausch, "Der Smekal-Raman Effekt," Julius Springer, Berlin, 1931, page 154] and the bending force constants for most bonds average about 0.6 × 10^5 dyne per cm. [D. H. Andrews, *Phys. Rev.*, **36**, 544 (1930)].

[26] "A Table of Dipole Moments," *Trans. Faraday Soc.* (1934). All observed moments quoted are taken from this table.

[27] There is no very decisive evidence in favor of this, but the non-polarity of even quite complex hydrocarbons, in which some distortion of the valency angles might be expected to occur, is some evidence and general considerations of electro-negativity point to the same conclusion.

From this it is quite clear that determinations of inter-covalency angle from the total moment of a compound AX_2 or AX_3 and the moment of the bond AX are liable to be seriously in error, especially if the bonds are very polarizable. Conversely, if the magnitude of the moment of the bond AX be calculated in such compounds, using the total moment and the correct angle, the value so found is likely to be very different from the value for the bond in a different environment, the difference being symbat with the polarizability of the atoms composing the bond. This is, unfortunately, a great difficulty in the way of attempts to make quantitative correlations of the moments of bonds with the relative electronegativities of the component atoms, such as that of Malone,[28] for it makes it necessary either to correct the moment to a standard environment or else to recognize that the effective electronegativity of the central atom, A, depends upon the number and the type of atoms with which it is combined.[29] It is not even satisfactory to compare the moments of bonds in similar types of compound, *e. g.*, those of the carbon–chlorine and arsenic–chlorine bonds in chloroform and arsenic trichloride, because the interactions of the bonds may be considerably different. These facts have already been recognized to some extent, but the present results strongly emphasize their importance.

We are deeply indebted to Professor Linus Pauling for much aid and encouragement in this investigation.

Summary

The molecular structures of chlorine monoxide, oxygen fluoride, dimethyl ether, and 1,4-dioxane as determined by electron diffraction methods (Table X) show that the oxygen valence angle is increased above its value in the water molecule when comparatively heavy groups are bonded to the oxygen. When these groups are chlorine or methyl, the increase is more than 5°. The observed carbon–oxygen bond distance is in agreement with the covalent radius sum, but the chlorine–oxygen distance is 0.06 Å. greater.

TABLE X

Bond	Bond distance, Å.	Angle	Radius sum,[2] Å.
Cl–O in Cl_2O	1.71 ± 0.02	111 ± 2°	1.65
O–F in OF_2	1.4 ± .1	105 ± 5°	1.30
C–O in $(CH_3)_2O$	1.44 ± .03	111 ± 4°	1.43
C–O in dioxane	1.46 ± .04	110 ± 5°	1.43
C–Cl in CH_3Cl	1.77 ± .02		1.76
C–Cl in CH_2Cl_2	1.77 ± .03	111 ± 2°	1.76
C–Cl in $CHCl_3$	1.78 ± .03	111 ± 2°	1.76
(C–Cl in CCl_4	1.760 ± .005	109°28′	1.76)

The results on the chlorinated methanes show that the carbon–chlorine bond distance is constant in this series and equal to the covalent radius sum to within the experimental error. The tetrahedral angle in carbon tetrachloride is increased by 2 or 3° in chloroform and methylene chloride.

These results are combined with the results of measurements of the electric dipole moments to show that the moment associated with the carbon–chlorine bond has in chloroform and methylene chloride not more than 70% of its value in methyl chloride. The magnitude of the mutual effect of dipoles in different bonds of the same molecule indicates the extreme care which must be used in interpreting dipole moment data.

PASADENA, CALIF. RECEIVED JANUARY 23, 1935

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[28] J. G. Malone, *J. Chem. Phys.*, **1**, 197 (1933); J. G. Malone and A. L. Ferguson, *ibid.*, **2**, 99 (1934).

[29] R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).