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Determination of Molecular Structure by Electron Diffraction

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(1) An apparatus has been designed and built for the purpose of determining molecular structure by electron diffraction using 6400 volt electrons. (2) The apparatus was checked with carbon tetrachloride whose structure is accurately known, and the interatomic distances in, and configurations of, a number of compounds determined. (3) Ethylene oxide was found to be a three membered ring with a carbon-carbon distance of $1.56 \pm 0.05\text{\AA}$, a carbon-oxygen distance of $1.45 \pm 0.05\text{\AA}$ and a carbon-hydrogen distance of $1.05 \pm 0.07\text{\AA}$. (4) Sulfur monochloride was found to have the two chlorine atoms attached to

different sulfur atoms, the sulfur-sulfur distance was found to be $2.04 \pm 0.05\text{\AA}$, the sulfur-chlorine distance of $1.98 \pm 0.05\text{\AA}$ and an angle of $105 \pm 5^\circ$ between bonds. (5) In acetaldehyde the carbon-oxygen distance was found to be $1.20 \pm 0.05\text{\AA}$, the carbon-carbon distance $1.51 \pm 0.05\text{\AA}$ and the bond angle $122 \pm 5^\circ$. (6) Paraldehyde was found to have a puckered ring structure with a carbon-oxygen distance of $1.41 \pm 0.05\text{\AA}$, a carbon-carbon distance of $1.52 \pm 0.05\text{\AA}$ and the tetrahedral angle of 109° between bonds.

SINCE the original work of Mark and Wierl,¹ the results of many investigators² have shown that electron diffraction methods provide a very useful tool for determining molecular structure. The object of the experiments reported here was to extend this work and to determine if much lower voltages (6500 volts instead of 20 to 50 kilovolts) might not be used in electron diffraction apparatus for determining molecular structure.

In the interpretation of the experimental results the complete formula for the coherent scattered intensity, given below, was not used. In this formula

$$I \propto \sum_{i,j} \psi_i \psi_j \frac{\sin x_{ij}}{x_{ij}}, \quad (1)$$

where

$$\psi_i = (Z_i - F_i)/\mu^2$$

and

$$x_{ij} = (4\pi \sin \frac{1}{2}\theta/\lambda)l_{ij} = \mu l_{ij}$$

Z and F being the atomic number and form factor for the i th atom, l_{ij} the distance between the i th and j th atoms, the summation being taken over all the atoms of the molecule. As Pauling and Brockway³ have pointed out, when

the maxima and minima of intensity are measured by visual means, as was done here, the simpler formula, given below, usually suffices.

$$I' \propto \sum_{i,j=1}^n Z_i Z_j \frac{\sin x_{ij}}{x_{ij}} \quad (2)$$

where $I' = I \cdot f(\theta)$ and $f(\theta)$ is a monotonic function of the angle, θ . The difference between the two formulae is greatest at small angles, and preliminary calculations with a model of ethylene oxide similar to that finally used gave for the positions of the first maximum by the two formulae of 4.17 and 4.21×10^{-8} , the difference being less than the experimental error. From the experimental curves given by Mott and Massey⁴ we may conclude that the scattering by single atoms is still proportional to $((Z_i - F_i)/\mu^2)^2$ for voltages as low as 2000 volts except for very heavy atoms or very large angles of scattering. Hence we may feel sure that our formula (1) and consequently (2) will be valid for the 6400 volts used.

DESCRIPTION OF APPARATUS AND METHOD

The general design of the apparatus follows that of Hendricks,⁵ except that a filament was used as a source of electrons rather than a discharge tube. The filament was a flat spiral of platinum wire coated with barium oxide, and

* Adapted from a thesis submitted to The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

¹ Mark and Wierl, *Physik. Zeits.* **31**, 366, 1028 (1930).

² Especially Pauling and his co-workers: Pauling and Brockway, *Proc. Nat. Acad. Sci.* **19**, 860 (1934); Brockway and Wall, *J. Am. Chem. Soc.* **56**, 2373 (1934); Sutton and Brockway, *J. Am. Chem. Soc.* **57**, 473 (1935); and also Dornte, *J. Chem. Phys.* **1**, 566, 602 (1933) and de Laszlo, *Proc. Roy. Soc. A* **146**, 672 (1934).

³ Pauling and Brockway, *J. Chem. Phys.* **2**, 867 (1934).

⁴ Mott and Massey, *The Theory of Atomic Collisions* (Oxford University Press, 1933), p. 122.

⁵ Hendricks, Maxwell, Moseley and Jefferson, *J. Chem. Phys.* **1**, 549 (1933).

was so mounted that it could be moved from outside the apparatus to give the best electron beam intensity. Eastman process plates were used to record the scattered electrons, but because of the slight effect of the low voltage electrons on the plates it was found advisable to oil them. The distance from the jet through which the gas issues to the photographic plate was 7.45 cm. The whole apparatus was mounted so that the path of the electron beam made an angle of 45 degrees with the horizontal and was in the direction of the earth's magnetic field so as to reduce the effect of this field on the beam as far as possible.

The high potential was secured from a 110-7000 volt transformer using two General Electric PJ-24 tubes for full wave rectification. The pulsations were smoothed out by means of a 0.5 microfarad condenser and a choke coil. The filament was heated by the current from another transformer and the filament temperature controlled by a variable resistance in the primary circuit of this transformer. The voltage applied across the apparatus was determined by measuring the current through a calibrated high resistance of eight megohms.

EXPERIMENTAL RESULTS

As a check on the apparatus and in order to become familiar with the interpretation of the actual photographs, it was decided to first study a compound whose structure was already known. Carbon tetrachloride was chosen for this because of the accurate data which are available for this compound. The C. P. material was distilled under a vacuum into the bulb from which it was to be vaporized and there several times alternately frozen and melted while under a vacuum to eliminate as much as possible of the dissolved air. During the run the material was kept at 0°C by means of an ice bath, and exposures of from 4 to 32 seconds were taken. The results are tabulated in Table I below. The experimental figures represent the average of measurements on twelve plates, the deviation of any measurement from the average being not more than two percent. The accelerating voltage was 6400 volts which corresponds to a wave-length of 0.1531Å. The calculated values are based on a chlorine-carbon distance of 1.77Å which compares very favorably

TABLE I. *Carbon tetrachloride.*

	VALUES OF $\mu \times 10^8$	
	Observed	Calculated
Maximum	2.71	2.69
Minimum	3.76	3.74
Maximum	4.80	4.79
Minimum	5.97	5.96
Maximum	7.16	7.16

with the value of 1.76Å found by Brockway and Wall² and by de Laszlo and Cosslet⁶ and the value of 1.78Å found by Braune and Knoke.⁷

Pauling and Brockway³ have indicated that the interatomic distances measured by electron diffraction can be used to calculate a series of covalent radii for the various atoms. Because of the fact that the structural formula for ethylene oxide is usually written as a three membered ring, it was thought that in this compound the carbon-oxygen distance might be slightly different from that in acyclic compounds. The ethylene oxide, taken from a commercial tank, was carefully distilled, the fraction taken for use having a boiling point range of less than one degree. The compound was kept at -40°C during the run, this temperature being found to give the optimum vapor pressure. Because of the small scattering power of ethylene oxide, exposures up to 300 seconds were necessary. The experimental values of μ are given in Table II and are the

TABLE II. *Ethylene oxide.*

	VALUES OF $\mu \times 10^8$	
	Observed	Calculated
Maximum	5.34	5.37
Minimum	7.46	7.48
Maximum	9.58	9.55

average of measurements on nine plates. The calculated values are based on a carbon-oxygen distance of 1.45Å and a carbon-carbon distance of 1.56. In compounds of low scattering power it may be necessary to take the scattering by the hydrogen atoms into account; this was done here using a carbon-hydrogen distance of 1.05Å and although the calculated values were not very sensitive to small changes in this distance, including these terms does have an appreciable

⁶ de Laszlo and Cosslet, *Nature* **134**, 63 (1934).

⁷ Braune and Knoke, *Zeits. f. physik. Chemie* **B21**, 297 (1933).

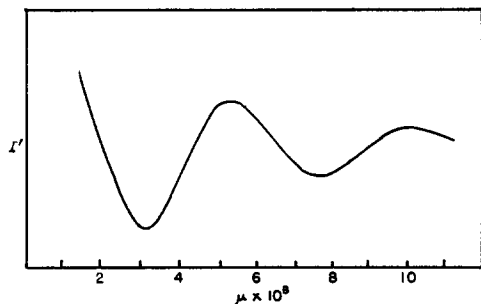
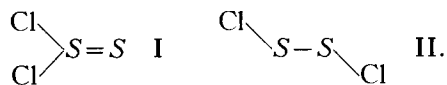


FIG. 1. Theoretical intensity curve for ethylene oxide.

effect. The theoretical intensity curve is given in Fig. 1. The carbon-carbon distance found above is in good agreement with the distance of 1.54Å found by Dornte.² The carbon-oxygen distance compares quite favorably with the distance of 1.44Å found by Sutton and Brockway² in dimethyl ether. These results, together with the fact that no alternative structure could be found which would give any agreement with the experimental points, indicates that ethylene oxide is a three-membered ring in which the interatomic distances are nearly the same as in acyclic compounds. Alternate structures in which the oxygen atom was at a greater distance from one carbon atom than from the other gave no agreement with experiment.

The structure of the compound, sulfur monochloride, is not definitely established. The available chemical evidence does not seem to be sufficient to distinguish between the two alternative structural formulae given below, though it does seem to favor formula II.



For this reason it was decided to study this compound by electron diffraction to see if more light could be thrown on the subject. Merck's sulfur monochloride was carefully distilled in a vacuum from a receiver containing a quantity of free sulfur and activated bone charcoal to remove impurities. The material was kept at 30°C during the runs and exposures of from 10 to 200 seconds were taken. The results, given below, are the average of measurements on eleven plates. The calculated values were obtained by using formula II, a chlorine-sulfur distance of

1.98Å, a sulfur-sulfur distance of 2.04Å and an angle of 105° between bonds. In the structure II for sulfur monochloride it is probable that there would be some free rotation about the sulfur-sulfur bond. Accordingly with the use of the above structure, distances, and angles, the theoretical curve was calculated for three different positions of the two chlorine atoms. In Table III,

TABLE III. *Sulfur monochloride.*

	Observed	VALUES OF $\mu \times 10^3$		
		A	Calculated B	C
Maximum	4.12	4.20	4.13	4.17
Minimum	5.55	5.44	5.50	5.44
Maximum	6.68	6.64	6.70	6.63
Maximum	7.83	8.10	7.86	7.60
Minimum	8.90	9.04	8.93	9.07
Maximum	10.21	10.27	10.16	10.32

A gives the values of μ when the shortest possible chlorine-chlorine distance consistent with the above structure was used, B the results when an average distance based on free rotation was used, and C the results when the longest possible distance was used. It will be noted that B agrees best with the experimental results. When similar calculations are carried out using different values for the sulfur-sulfur and sulfur-chlorine distances, the results obtained do not agree at all with experiment for any relative positions of the atoms. The theoretical intensity curve for this structure is given in Fig. 2.

While these results are not in such good agreement with the values of 2.05 and 2.10Å, respectively for the two distances which one would obtain by the use of Pauling and Huggins⁸ table of covalent radii, they are in favor of the second of the two formulae given for sulfur monochloride.

Acetaldehyde and its polymer, paraldehyde, were also studied. The acetaldehyde was prepared by distilling it from C. P. paraldehyde to

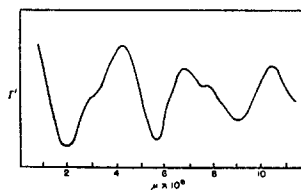


FIG. 2. Theoretical intensity curve for sulfur monochloride.

⁸ Pauling and Huggins, *Zeits. f. Krist.* **87**, 205 (1934).

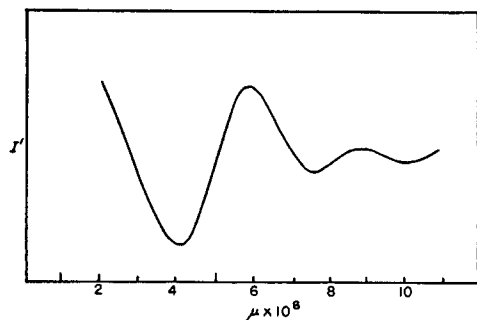


FIG. 3. Theoretical intensity curve for acetaldehyde.

which a few drops of sulfuric acid had been added. The runs were made in the usual manner. The material was kept at -35°C in the bulb and exposures up to 300 seconds were taken. The results, Table IV, are the averages of measurements on ten plates. The theoretical intensity curve is given in Fig. 3. The calculated values were obtained by using a carbon-carbon distance of 1.51Å, and oxygen-carbon distance of 1.20Å and an angle of 122° between the two bonds. Due to the fact that only two maximum could be measured, the structure could not be determined uniquely, but that given does show good agreement with the experimental measurements and with other measurements of these distances.

For paraldehyde the runs were made in the usual manner, the material being kept at 30°C during the runs and exposures up to 200 seconds were taken. The results, Table V, are the averages of measurements on eleven plates.

For the calculation of the values of μ tabulated in Table V and the theoretical curve given in Fig. 4, a structural formula must be assumed for

TABLE IV. *Acetaldehyde*.

	VALUES OF $\mu \times 10^3$	
	Observed	Calculated
Maximum	5.92	5.91
Minimum	7.60	7.61
Maximum	8.74	8.72

TABLE V. *Paraldehyde*.

	Observed	VALUES OF $\mu \times 10^3$	
		A	B
Maximum	3.40	3.43	3.44
Minimum	4.41	4.45	4.20
Maximum	5.69	5.67	5.79
Minimum	7.47	7.46	7.47
Maximum	9.24	9.22	9.16

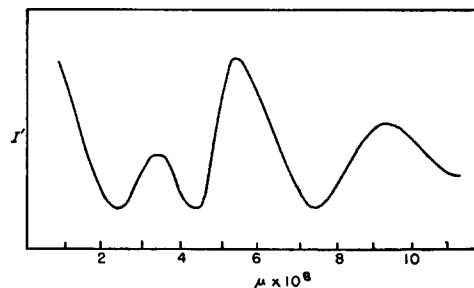
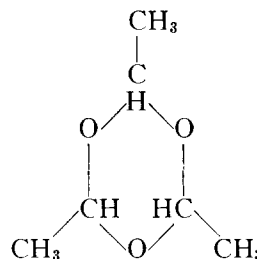


FIG. 4. Theoretical intensity curve for paraldehyde.

the molecule. The one used is the usual ring formula for paraldehyde with a puckered ring, i.e., the carbon and oxygen atoms are not all in the same plane. The carbon-oxygen distance was taken to be 1.41Å, the carbon-carbon distance as 1.52Å with the angle between the bonds the tetrahedral angle of $109^{\circ}28'16''$. The relative positions of all the carbon and oxygen atoms is given by the statement that if the plane formula



be taken as the projection of the molecule on the plane of the paper, the projected ring would form a regular hexagon, and that if the ring carbon atoms were in the plane of the paper, the oxygen atoms would be a distance of $1.41 \times \sin 19^{\circ}28'16'' = 0.47\text{Å}$ above this plane and the three methyl carbon atoms a distance of $1.52 \times \sin 19^{\circ}28'16'' = 0.51\text{Å}$ above this plane. The formula used to calculate the intensity then becomes

$$I \sim 576 \left[\frac{\sin 1.41\mu}{1.41\mu} + \frac{\sin 2.3932\mu}{2.3932\mu} \right] + 600 \frac{\sin 2.3025\mu}{2.3025\mu} \\ + 432 \frac{\sin 3.6506\mu}{3.6506\mu} + 288 \left[\frac{\sin 2.7186\mu}{2.7186\mu} + \frac{\sin 4.0919\mu}{4.0919\mu} \right] \\ + 216 \left[\frac{\sin 1.52\mu}{1.52\mu} + \frac{\sin 4.7847\mu}{4.7847\mu} \right].$$

This structure gives the values of μ for the maxima and minima marked A in the table. If we use the similar structure in which the

methyl carbon atoms are directly below the other carbon atoms a distance of 1.52Å, we get the values of μ marked *B* in the table. The difference is not very marked but it is sufficient to make it probable that the methyl carbon atoms are, as we have sketched them, above the plane of the oxygen atoms.

DISCUSSION OF RESULTS

While an apparatus has been developed by which one may make measurements of interatomic distances by means of the diffraction of electrons of only 6400 volts energy, the accuracy of the results is not as great as that of other workers using higher voltages. In the experiments reported here, the accelerating voltage was known with an accuracy of one percent. The ammeter and resistance used were thus accurate, the choke coil and condenser were sufficient to smooth out the pulsations of the rectified 60-cycle alternating current to this degree of accuracy, and the actual measurements showed that the variations in the input alternating current were no greater than this.

The distance from the jet to the photographic plates could be measured quite accurately, the error here being certainly less than one percent.

The greater error is in the actual measurement of the positions of the maxima on the plates. This is especially true since the maxima are not sharp lines but are rather broad. The fact that the measurements from the individual plates do not differ from the average by more than 3 percent indicates that the maxima can be determined fairly accurately. The final values of μ are probably accurate to within two percent. The relation between the positions of the maxima and the values of the interatomic distances is, in general, quite complicated, so that for a given error in the former it is difficult to estimate the error in the latter.

A real source of error in these experiments comes from the fact that only a few maxima and minima could be measured due to the limitations of the apparatus. When this is true, the fact that the observed and calculated values of μ agree very well is not a guarantee of like accuracy in the values of the interatomic distances. For small variations in the structure are best detected in the positions of the outer maxima, those beyond the third. It is difficult to say just how much effect this would have on the compounds studied here, but it is probable that the measurements recorded are accurate to $\pm 0.05\text{\AA}$.

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The Application of the Three-Dimensional Patterson Method and the Crystal Structures of Proustite, Ag_3AsS_3 , and Pyrargyrite, Ag_3SbS_3 *

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(Received March 18, 1936)

It is shown that the three-dimensional Patterson method can be so simplified by the use of the symmetry properties of the crystal under consideration that its use in determining the positions of atoms in crystals is practicable. This method is then used to determine the positions of the heavy atoms in proustite, Ag_3AsS_3 . The positions of the sulfur atoms are found by the use of the covalent atomic radii and assumptions concerning bond directions. The structure so derived is found to be compatible with the observed data. Proustite is found to contain pyramidal AsS_3''' groups and silver atoms forming two bonds to sulfur in almost opposed directions. Pyrargyrite, Ag_3SbS_3 , is found to have almost the same structure as proustite. The analytical statement of the structures is as follows:—The space group, C_{3v}^6-R3c , is common to both proustite and pyrargyrite. The special positions of C_{3v}^6 are (in

hexagonal axes)

$$(2a) \quad 0, 0, Z; \quad 0, 0, \frac{1}{2} + Z;$$

$$(6b) \quad \begin{array}{lll} X, Y, Z; & \bar{Y}, X-Y, Z; & Y-X, \bar{X}, Z; \\ \bar{Y}, \bar{X}, \frac{1}{2} + Z; & X, X-Y, \frac{1}{2} + Z; & Y-X, Y, \frac{1}{2} + Z; \end{array}$$

and positions derived from these by the operations of the rhombohedral lattice. The parameter values are:

Proustite		Pyrargyrite	
$a_0 = 10.74\text{\AA}$,	$c_0 = 8.64\text{\AA}$	$a_0 = 11.04\text{\AA}$,	$c_0 = 8.71\text{\AA}$
2As in $2a$,	$Z_{\text{As}} = 0.000$	2Sb in $2a$,	$Z_{\text{Sb}} = 0.000$
6Ag in $6b$,	$X_{\text{Ag}} = 0.246$	6Ag in $6b$,	$X_{\text{Ag}} = 0.250$
	$Y_{\text{Ag}} = 0.298$		$Y_{\text{Ag}} = 0.305$
	$Z_{\text{Ag}} = 0.235$		$Z_{\text{Ag}} = 0.210$
6S in $6b$,	$X_{\text{S}} = 0.220$	6S in $6b$,	$X_{\text{S}} = 0.220$
	$Y_{\text{S}} = 0.095$		$Y_{\text{S}} = 0.105$
	$Z_{\text{S}} = 0.385$		$Z_{\text{S}} = 0.355$