Part I

Some Investigations of Molecular Structures

by the Electron Diffraction Method

Part II

On the Ultraviolet Absorption Spectrum of Ozone

Thesis

by

William Shand, Jr.

In Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy

California Institute of Technology Pasadena, California, 1946

Contents

Part	I.	• Some Investigations of Molecular Structures by the Electron Diffraction Method					
	A.	Preparation of Electron Diffraction Photographs and their Interpretation by the Visual Method	1				
	Β.	The Structures of Methylenecyclobutane and 1-Methylcyclobutene	9				
	с.	The Molecular Structures of some Heterocyclic Compounds	14				
		 (a) Trimethylene oxide (b) Ethylene Methylene Dioxide (c) Dioxane-1,4 (d) Trioxane (e) Pyrazolidine (f) 1,2-Trimethylenepyrazolidine 	16 22 27 32 37 42				
	D.	The Molecular Structures of Ozone and Ozonides	50				
		 (a) Ozone (b) Dimethylperoxide (c) Ethylene Ozonide and 2-Butene Ozonide 	50 58 67				
-	E.	The Molecular Structures of some Halogenated Ethanes	89				
		 (a) Methyl Fluoroform (b) Methyl Difluorochloromethane (c) Methyl Fluorodichloromethane (d) dl- and meso-2,3-Dichlorobutane 	89 94 99 105				
		References	113				
Part	II.	On the Ultraviolet Absorption Spectrum of Ozone	118				
		References	132				
Summ	ary		134				
Ackn	owled	dgements	135				

Part I

Some Investigations of Molecular Structures by the Electron Diffraction Method

Some Investigations of Molecular Structure by the Electron Diffraction Method

Of all the methods of investigating the molecular configurations of gaseous substances, the electron diffraction method is at present the most powerful. It gives in principle a means of determining directly without any add tional assumptions the internuclear distances in molecules. These distances may be correlated with geometrical models of the arrangements of the atoms of the molecule, and by comparison of the observed and calculated intensities of scattering of the electrons for various models, conclusions regarding the structure of the molecule may be drawn. In Part I of this thesis are described the results of investigations of a number of gaseous molecules by the electron diffraction method.

Preparation of Electron Diffraction Photographs and their Interpretation by the Visual Method.

The experimental procedure used in producing the electron diffraction photographs is in general that of Brockway (1,2). Briefly, electrons emitted from a hot tungsten filament are accelerated by a potential drop of about 40,000 volts, and after passing through a collimating pinhole system, intersect a fine jet of the gaseous substance under investigation. The electrons are scattered by the gas with an intensity dependent on the angle of scattering relative to the primary beam of electrons, and characteristic of the structure of the gas molecules. The electrons then pass on and are recorded photographically at a fixed distance from the point of scattering. The photographs produced in this manner have heavy blackening around the image of the central beam, surrounded by what appear to be diffuse concentric rings. The intensity of blackening falls off rapidly from the center towards the edge of the film.

The theoretical expression (1) for the intensity I(s) of fast electrons scattered into unit solid angle per unit of time is:

$$\mathbf{I}(s) = K\left\{\sum_{i} f_{i}^{2} + \sum_{i} \sum_{j} f_{i} f_{j} \frac{\sin sr_{ij}}{sr_{ij}} e^{-A_{ij}} + \sum_{i} \frac{S_{i}}{s^{4}}\right\}$$
(1)
$$i \neq j$$

The various symbols in this expression are defined as follows:

- $s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$ $\lambda = \text{wave-length of the electrons, determined by scattering from gold foil or zinc oxide smoke (11)'
 <math display="block">f_{i} = \frac{Z_{i} F_{i}}{s^{2}}$ $Z_{i} = \text{atomic number of the i-th atom.}$
- $F_{i} = 4\pi \int_{0}^{\infty} |\phi(r)|^{2} \left(\frac{\sin sr}{sr}\right) r^{2} dr \qquad \text{the atomic scattering factor,}$

which has been tabulated for all atoms (3)

r = internuclear distance of the i-th and j-th atoms of the
molecule.

 $S_i =$ tabulated inelastic scattering factor (4) for the i-th atom.

e^{-A}ij=temperature factor (5), discussed below.

The summations extent over all atoms in the molecule. The first and last terms in the expression for I(s) decrease rapidly and monotonely with increasing s, and are of no interest in the determination of

structure. The double summation contributes a fluctuation above and below the rapidly decreasing general background. Microphotometer traces of photographs show that the visually apparent maxima and minima are really only fluctuations on the steeply falling background intensity (6).Since the eye is sensitive to changes of intensity relative to the background rather than to the absolute value of the intensity, the theoretical expression is usually modified to approximate the visual appearance of photographs. The first step in the "visual method" of interpretation (7,6) consists in drawing a representation of the visual appearance of the photographs in which the monotonely decreasing background is ignored, and only the structure sensitive fluctuating terms are considered. The attempt is made to represent by the visual curve the appearance of the molecular scattering when calculated on the basis of a simplified theoretical intensity function for the correct molecular model. The "simplified theoretical intensity function" used in these laboratories (6, 10d) is

$$I'(q) = K \sum_{i} \sum_{j} \frac{(z_{i} - F_{i})(z_{j} - F_{j'})}{(z - F)^{2}} e^{-A_{ij}} \sin(\frac{\pi}{10} \tau_{ij}q)$$

$$i \neq j$$
(II)

Here K is an arbitrary constant, $q = \frac{10}{\pi}S = \frac{40}{\lambda}\sin\frac{\theta}{2}$, a quantity chosen for convenience in the calculations with punched cards on International Business Machines, and $(Z - F)^2$ is the average of $(Z_i - F_i)^2$ taken over all the atoms in the molecule. The first maximum of (II) is not observable as such, so that an estimate of its position and height is usually made from previous experience. Fortunately this peak is not of great importance in influencing the final choice of the

-3-

best structure or in constructing the radial distribution function. It is very important to produce as complete and detailed a visual curve as possible before calculating any theoretical curves. If necessary any features of doubtful appearance may be referred to similar features on photographs of substances whose structures are known.

After the visual curve has been drawn in accordance with experience with the visual method, two procedures are generally followed. First, a "radial distribution function" is calculated (8). If the molecule is considered as having a continuous distribution of scattering power, the expression for I'(q) can be written

$I'(q) = K' \int_{0}^{\infty} \frac{r^2 D(r)}{r} \sin\left(\frac{\pi}{10} rq\right) dr$

in which $r^2D(r)$ represents the product of scattering powers of all elements of volume separated by distance r. This is a Fourier Integral and can be inverted to give

$$TD(T) = K'' \int_0^\infty I'(q) \sin(\frac{\pi}{10} rq) dq$$

Since the experimental data do not in general extend beyond q = 80-100, the convergence of the integral is improved by the introduction of an "artificial temperature factor" e^{-aq^2} , which is chosen so that $e^{-aq^2_{max}} = 0.10$ (9). For convenience in calculation the integration is approximated by a summation, so that the expression used to calculate the radial distribution function is:

$$\tau D(\mathbf{r}) = \sum_{q_{\mathbf{k}}=0}^{q_{\mathbf{max}}} \mathbf{I}'(q_{\mathbf{k}}) e^{-aq_{\mathbf{k}}^{2}} \sin\left(\frac{\pi}{10}q_{\mathbf{k}}\mathbf{r}\right) \Delta q \qquad (III)$$

In practice a plot of the visual curve is divided into about a hundred equal segments for which $\Delta q = 1$. The value of $I'(q_{k})e^{-aq_{k}^{2}}$ at each endpoint is computed, and the summation made in the same manner as with the theoretical intensity curves. The absolute numerical value of $I'(q_{k})$ is arbitrary, being chosen so that the general amplitude of the visual curve will approximate that of the simplified theoretical curves for the molecule. The peaks of the radial distribution curve are interpreted as internuclear distances in the molecule, and are used as a guide in selecting proper models for the molecular structure.

After possible or probable models have been chosen on the basis of the radial distribution function, the "correlation procedure" (6) is employed to determine the finer details of the structure, and the allowed range of parameter variation. The correlation procedure originally consisted in calculating simplified theoretical intensity curves for all reasonable models of the molecular structure, and comparing these with the visual curve. Since more reliance can usually be placed upon the improved radial distribution "integral", the procedure is considerably shortened, and fewer curves for comparison need be calculated. Curves which agree in detail with the visual curve, and which arise from molecular models which account for the radial distribution peaks, must be considered satisfactory as far as the electron diffraction experiment is concerned. In some cases the satisfactory structure will be unique; in others the ambiguity may be resolved by other structural or chemical information; but in many cases no decision among two or more acceptable

models can be reached. After the best agreement relating observed visual curve and theoretical curves has been found, quantitative comparison of observed and calculated q values for the maxima and minima of the visual curve fixes the size of the molecule. Some estimate of the range of allowed parameter variation is usually made by the correlation procedure. The shape parameters of the molecule are varied in the neighborhood of the "best" values until the resulting curves are no longer acceptable as representing the visual curve. In the simplest case of a diatomic molecule the theoretical curve consists of one $\sin \frac{\pi}{10}$ for values fixes the size (or "scale") of the molecule within the experimental errors of the method of making the photographs, and the observational errors of measuring them.

It is true that even in this simplest case considerable practice and comparison with values obtained from other sources (spectroscopy, x-ray investigations) is often necessary before the observational errors are minimized.

With complicated molecules (more than one parameter) no <u>exact</u> significance can be attached to the "limits of error" reported by the investigator. The interpretation of the range of allowed parameter variation is that this range encompasses the limits outside of which the investigator is certain he finds definite disagreement with the visual curve. It may still be possible to distinguish between the theoretical intensity curves and the visual appearance of the electron

-6-

diffraction photographs within the limits noted, and the exact choice of these limits will accordingly always be somewhat indefinite, and vary from investigator to investigator.

In calculating the simplified theoretical curves by the use of expression (II) it is sufficiently accurate for molecules composed of light atoms (H, C, N, O, F) or atoms of the same row in the periodic table to replace the factors $(Z_i - F_i)$ of Equation II by Z_i , the coefficients $(Z_{i}-F_{i})(Z_{j}-F_{j})/(Z-F)^{2}$ being nearly enough independent of s so that they become approximately proportional to ZiZj. Hydrogen must be given an effective Z value of 1.25, which is appropriate for s \angle 15, and tolerable for s > 15 because of the hydrogen term temperature factors. Z; for other atoms is simply the atomic number. This approximation was used for all calculations except for dichlorobutane (page). where $(Z_i - F_i)$ values were used. The temperature factor $e^{-\Delta i}j$ has the theoretical value $e^{-\left\{\frac{\overline{\delta l_{ij}}^2}{2}\left(\frac{\pi}{10}q\right)^2\right\}}$ where $\overline{\delta l_{ij}}^2 = \sum_{n=1}^{\infty} \left(\overline{\delta l_{ij}}\right)_n^2$ is the sum of the squares of the mean displacements of the i-th and j-th atoms relative to each other, due to thermal vibration (5). If $A_{i,j} = a_{i,j}q^2$ the value of $a_{i,j}$ has been estimated roughly (10) for hydrocarbons to be about 0.00015 for bonded C-H terms, and 0.0003-0.00045 for non-bonded X · · H terms. These values include a correction to correspond to factoring out the heavy-atom term temperature factors, for which in the actual calculations aij is set equal to zero. In calculating the theoretical intensity curves described in this thesis all C-H bonded terms were included with a = 0.00015. All X ··· H terms in which the

H atom was separated from the X atom by not more than two other atoms were included with $a_{ij} = 0.0003$. Longer X...H terms were either interpolated visually to about q = 30, or neglected. No H...H terms were considered. Further special assumptions used in calculating the simplified theoretical intensity curves are described under the appropriate compound. All summations were carried out with punched cards on International Business Machines.

$[{\rm Contribution\ from\ the\ Gates\ and\ Crellin\ Laboratories\ of\ Chemistry,\ California\ Institute\ of\ Technology,} No.\ 950]$

The Structures of Methylenecyclobutane and of 1-Methylcyclobutene

BY W. SHAND, JR., VERNER SCHOMAKER AND J. RODNEY FISCHER

The hydrocarbon prepared by Gustavson¹ by the action of zinc dust on pentaerythrite tetrabromide has been subjected to an intensive chemical investigation² on the basis of which structure (I) has been assigned to this substance. The struc-



ture may be regarded as definitely established in spite of the appearance of a recent article by Rogowski,³ who advocated the spiropentane^{3a} structure (II) on the basis of electron diffraction studies. A more recent electron diffraction investigation by Bauer and Beach⁴ with results in essentially complete disagreement with those of Rogowski is compatible with structure (I) and eliminates structure (II). The hydrocarbon (III) was also first obtained by Gustavson.⁵ It is not as readily accessible as (I) and consequently has received less attention from chemists; its structure, however, is not in doubt.²

(1) Gustavson, J. prakt. Chem., [2] 54, 97 (1896).

(2) More pertinent references: Demjanow, Ber., 41, 915 (1908); Faworsky and Batalin, *ibid.*, 47, 1648 (1914); Philipow, J. prakt. Chem., [2] 93, 162 (1916); Demjanow and Dojarenko, Ber., 55, 2718, 2727 (1922). The last paper cited demonstrates the identity of the Gustavson hydrocarbon with methylenecyclobutane independently synthesized by a method indicative of structure.

(3) Rogowski, Ber., 72, 2021 (1939). Structure (II) had previously been advanced in the earlier part of the chemical investigation, but the facts cited in its favor proved on closer examination to be without foundation: Fecht, Ber., 40, 3883 (1907), cf. Mereschkowski, J. Russ. Phys.-Chem. Soc., 46, 517 (1914) [Chem. Abst., 8, 3187 (1914); Chem. Zentr., 85, II, 1266 (1914)]; Zelinsky, Ber., 46, 160 (1913), cf. Philipow, loc. cit., Ingold, J. Chem. Soc., 123, 1706 (1923).

(3a) A third C₃H₈ hydrocarbon from pentaerythrityl bromide, not identical with either of the Gustavson hydrocarbons discussed in this paper, was recently reported by M. J. Murray and E. H. Stevenson and assigned to formula (II); THIS JOURNAL, 66, 314 (1944).

(4) S. H. Bauer and J. Y. Beach, THIS JOURNAL, 64, 1142 (1942).
(5) Gustavson, J. prakt. Chem., [2] 54, 104 (1896).

The present investigation was undertaken with the aim of isolating methylenecyclobutane and 1methylcyclobutene in a state as pure as possible and verifying their structures by the electron diffraction method. It was found, however, that the two compounds cannot readily be distinguished from each other by electron diffraction studies alone, and a determination of only some of the structural details was made, the others being assumed to correspond to the chemically established identity of each compound. The preparation and physical constants of methylenecyclobutane and 1-methylcyclobutene are accordingly described in some detail.

Preparation of Methylenecyclobutane.6-Crude pentaerythrityl bromide was made by the procedure in "Organic Syntheses." Five moles of pentaerythrytol was converted in a single operation to tetrabromide which was washed with water and 95% ethanol7 and air-dried, average yield 88%. The apparatus used for the hydrocarbon preparation consisted of a 12-liter flask fitted with a three-neck adapter carrying a dropping funnel, mercury-sealed stirrer, and a 38-cm. column without packing equipped with a cold finger at the top and connected to an ice-water cooled condenser; the receiver was surrounded with ice. An intimate mixture of 776 g. (2 moles) of crude tetrabromide and 785 g. (12 moles) of zinc dust was placed in the flask and one liter of water *cautiously* added. The mixture was heated to 85° on a water-bath and 500 cc. of ethanol was added portionwise (cf. Philipow, loc. cit.) with stirring over a period of two hours or until no more hydrocarbon distilled; frothing was controlled by raising or lowering the stirrer. At the end of the reaction the bath temperature was raised to 95° , forcing over the last traces of hydrocarbon together with some alcohol. The distillate was washed with two 100-cc. portions of water and dried over calcium chloride at 0°, yield 115 g. In a series of runs the yield varied between 70 and 90%. A quantity of the crude hydrocarbon (1340 g.) was twice fractionated through a 22-mm. inside diameter column, 6.5 ft. long, packed with glass helices and fitted with a total reflux, variable take-off

(6) The preparations described here were carried out by J. R. F. For details see his Masters' Thesis, California Institute of Technology, 1941.

(7) Schurink in "Organic Syntheses," Vol. 17, p. 73, J. Wiley, and Sons, Inc., New York, N. Y., 1937.

April, 1944 The Structures of Methylenecyclobutane and of 1-Methylcyclobutene 637

head. About 80% of the distillate⁸ boiled at 41.0-41.7° at 750 mm.; this material was refractionated a third time through a 3-foot column packed with helices and a middle portion reserved for electron diffraction study, b. p. 41.39° at 750 mm., n^{10} p 1.4266, n^{15} p 1.4236, n^{20} p 1.4210, d^{20} , 0.7401, d^{25} , 0.7349. The product obtained by Whitmore and Williams and used by Bauer and Beach, and identified as methylenecyclobutane by ozonolysis had the constants

b. p. 41.3° at 746 mm., a²⁰p 1.4203-6. Preparation of 1-Methylcyclobutene.—Although Philipow² claimed to have fractionated this hydrocarbon from the mixture obtained on treating pentaerythrite tetrabromide with zinc dust, the presence of a constant boiling fraction in this range could not be detected.⁹ Several unsuccessful attempts were made to prepare methylcyclobutene by isomerization of methylenecyclobutane over an alumina catalyst at 300°. The greater part of the hydrocarbon was converted to lower boiling

material but apparently this consisted almost entirely of products of ring-splitting.¹⁰ Attempts to dehydrate 1methylcyclobutanol^{5,6,11} were also unsuccessful; the use of 60% sulfuric acid and of anhydrous oxalic acid gave polymers while the tertiary alcohol was recovered unchanged after refluxing with iodine.

1-Chloro-1-methylcyclobutane was prepared in 80% yield by treating methylenecyclobutane with excess concentrated aqueous hydrochloric acid at 0°. After shaking for one hour, the lighter phase was washed with sodium carbonate solution, dried over calcium chloride and distilled, b. p. 90-91° at 745 mm., n^{20} D 1.4311, n^{25} D 1.4288, d^{20}_4 0.9495, d^{25}_4 0.9444. The corresponding bromide was prepared in 72% yield from methylenecyclobutane and 62% aqueous hydrogen bromide at 0°, mixing by hand at first and then shaking mechanically for one hour. The bromide layer was worked up in the above manner, b. p. 55-57° at 100 mm., n^{20} D 1.4698, n^{25} D 1.4673, d^{20}_4 1.3179, d^{25}_4 1.3110. 1-Jodo-1-methylecyclobutane was prepared by shaking 68 g. (1 mole) of methylenecyclobutane in a glass-stoppered bottle with a solution of 154 g. (1.2 moles) of hydrogen iodide in 200 g. of glacial acetic acid at 0°.⁵ The reaction mixture was poured into one liter of water, the heavy phase separated and washed with bisulfite and carbonate solutions and finally with water, crude yield 94%. At 20 mm. the product boiled at 40-42°, n^{25} D 1.5215, d^{20}_4 1.604, yield 76%. The chloride, bromide, and iodide were added dropwise

The chloride, bromide, and iodide were added dropwise under identical conditions to a 100% excess of a boiling solution of potassium hydroxide dissolved in cellosolve (ethylene glycol monoethyl ether). The mixed hydrocarbons produced were collected (yields from chloride 40%, bromide 60%, iodide 60%) and roughly analyzed by comparison⁶ of densities and refractive indices with the values found for the pure hydrocarbons. The material obtained from the chloride and from the bromide contained methylenecyclobutane and 1-methylcyclobutene in a ratio of about 2:1, while in the case of the mixture obtained from the iodide, the reverse ratio obtained.

A modification of the original method of Gustavson⁵ was therefore employed for the preparation of 1-methylcyclobutene in quantity. Fifty-six grams (1 mole) of potassium hydroxide was dissolved in 250 cc. of cellosolve (cellosolve gave higher yields than ethanol or ethanol-water) and this solution heated to boiling in a 500-cc. flask fitted with dropping funnel and reflux condenser through which water at 45° was circulated. The outlet at the top of the condenser led to another condenser set for downward distillation which was cooled by ice-water and then into a receiver cooled in a dry-ice bath. Ninety-eight grams (0.5 mole) of crude tertiary iodide was added dropwise over a period of two hours to the refluxing alkali solution and the hydrocarbon product washed with ice-water and dried over magnesium perchlorate, yield 20.4 g. The crude hydrocarbon mixture (233 g.) from several of the above experiments was fractionated twice through

The crude hydrocarbon mixture (233 g.) from several of the above experiments was fractionated twice through the 6.5 ft. column described previously, using, because of the small amount of material available, a higher boiling hydrocarbon still-base. A third fractionation was carried out using a spinning band column similar to the one described by Baker, et al.¹² This column had the equivalent of 18 theoretical plates at the reflux rate and throughput used. The considerable portion of material which boiled at 37-38° at 748 mm. in this third fractionation was fractionated again with the spinning band column to obtain material of constant refractive index, b. p. 37.1° at 750 mm., n^{18} p 1.4088, d^{20} , 0.7244, d^{25} , 0.7188. This material was used for the electron diffraction investigation.

Electron Diffraction Investigation

Experimental.—The electron diffraction apparatus used in this investigation has been described by Brockway.¹³ The camera distance was 10.89 cm., and the wave length of the electrons, determined from transmission photographs of gold foil, was 0.0615 Å. The photographs, made with the samples at about 25°, showed eight maxima and minima extending to s_0 values of about twenty-nine.

Interpretation.—Both the radial distribution method¹⁴ and the correlation method¹⁵ were used in interpreting the electron diffraction photographs. The radial distribution curves were calculated according to the formula where $I(s_k)$

$$rD(r) = \sum_{k} I(s_k)e^{-as_k^2} \sin s_k r$$

is a visually estimated intensity assuming no falling off of intensity with s_k , and a is chosen so that $e^{-as_{\max}^2} = 0.10$. A plot of the visually estimated intensities was divided into about 50 segments, and the $I(s_k)$'s taken at each endpoint.¹⁶

Theoretical intensity curves were calculated using the simplified theoretical scattering formula

$$I(s) = \sum_{i} \sum_{j} Z_{i} Z_{j} \frac{\sin r_{ij}s}{r_{ij}} e^{-a_{ij}s^{2}}$$

The constant a_{ij} in the exponential temperature factor term was given the value 0.002 for bonded C—H terms, 0.004 for non-bonded C—H terms, and 0.0 for all C—C terms. The contribution of C—H terms is important out to about s = 20.

Methylenecyclobutane.—The radial distribution curve shown at the top of Fig. 1 can be interpreted on the basis of a model with structure (I). Peaks occur at 1.09 Å., corresponding to the C—H bond, 1.55 Å., the C—C single-bond distance, 2.20 Å., the cross-ring distance, and 2.61 Å.,

(12) Baker, Barkenbus and Roswell, Ind. Eng. Chem., Anal. Ed., 12, 468 (1940).

(13) L. O. Brockway, Rev. Modern Phys., 8, 231 (1936).

(14) L. Pauling and L. O. Brockway, THIS JOURNAL, 57, 2684 (1935).

(15) L. Pauling and L. O. Brockway, J. Chem. Phys., 2, 867 (1934).
(16) R. A. Spurr and V. Schomaker, THIS JOURNAL, 64, 2693 1942).

⁽⁸⁾ Regarding the composition of the forerun see footnote (5) of reference (4).

⁽⁹⁾ Investigators other than Philipow obtained methylcyclobutene by the original Gustavson method, *cf.* for example Dojarenko, ref. (10).

⁽¹⁰⁾ Compare Dojarenko, Ber., 59, 2933 (1926).

 ⁽¹¹⁾ Demjanow and Dojarenko, J. Russ. Phys.-Chem. Soc., 45, 176
 (1913) [Chem. Abst., 7, 2226 (1913); Chem. Zentr., 84, I, 2027 (1913)].
 The observed constants were b. p. 115-118° at 747 mm., n²⁴ D 1.4333, d²⁴, 0.8971, m. p. -6 to -3°, solubility 1 part in 6.5-7 parts water at 25°, phenylurethan m. p. 139.9° (cor.) from isopropyl ether.

W. SHAND, JR., VERNER SCHOMAKER AND J. RODNEY FISCHER



the distance between the side-chain carbon and the non-bonded adjacent ring carbon atom. The double-bond distance is not resolved, although a small inflection occurs at 1.33 Å. The spiropentane structure (II) as reported by Rogowski³ can be ruled out, since it would give only two main peaks, at about 1.54 and 2.87 Å. Other structures differing widely from (I) with respect to their interatomic distances can likewise be ruled out by comparison with the radial distribution function. The chemical identification was accordingly accepted, and theoretical intensity curves calculated for structure (I).

Certain simplifying assumptions were made to reduce the number of structural parameters. The C-H bond distances were taken to be 1.09 Å., and the H-C-H angle on the ring to be 116°. The plane of these H-C-H's was perpendicular to the ring plane and bisecting the ring angles. Moreover, the carbon atoms were assumed to be coplanar and the C-C single-bond distances were taken as being all alike, reducing the problem to one of three parameters, namely, the C-C singlebond distance, the C-C double-bond distance, and an angle of the ring. The single-bond distance was taken from the radial distribution curve to be 1.55 Å., while the double-bond distance and the \angle C₄C₁C₂ were varied in calculating the theoretical intensity curves. Curves calculated for values of $\angle C_4C_1C_2$ varying from 87.5° to 100° with a double-bond distance of 1.34 Å. are shown in Fig. 1. The characteristic features of the observed pattern are the roundedness of the first maximum, the shelf-like appearance of the fourth maximum, the roundedness and almost complementary asymmetry of the sixth and seventh maxima. The eighth maximum (not shown) was a sharp peak whose position varied little from curve to curve. Best agreement is given by the curve marked 92.5°. The non-bonded $C \cdots C$ distances in this model are 2.14, 2.24, 2.65 and 3.48 Å.; most of the important C ··· H distances fall at about 2.20 Å. These distances and their relative weights are shown with the radial distribution curve in Fig. 1. Curves calculated with double bond distances of 1.30 and 1.38 Å. do not give as good agreement with the observed pattern. In general the second minimum is raised, the sixth maximum becomes more symmetrical, and the seventh maximum asymmetrical on the inner side instead of the outer side. Best agreement for these curves is found for $\angle C_4C_1C_2 = 90^\circ$ and C==C = 1.30Å. This is to be expected since for these values of the parameters the distances $C_5 \cdots C_2$, $C_5 \cdots C_4$, and $C_5 \cdots C_3$ are the same as for the 92.5° model with C = C = 1.34 Å. The main difference arises in the cross-ring distances, which are different in the 92.5° model, and alike in the square model.

The effect of removing the restrictions that the ring be coplanar, and that the C-C single-bond distances be all alike was investigated, these variations being made separately. Curves were calculated in which the C_5 , C_1 , C_2 and C_4 atoms were coplanar (as in ethylene), and the C₃ atom moved perpendicular to this plane. Curves were also calculated for coplanar models with C-C single-bond distances adjacent to the double bond different from those opposite the double bond. Although these theoretical curves showed small but definite points of disagreement with the observed pattern, especially at the second minimum and the sixth and seventh maxima, it became evident that with the available data the complete correlation procedure with the admission of these additional variations could not be made to give more precise information than was already available from the radial distribution function. The final parameter determination was accordingly carried out with the assumptions mentioned in the preceding paragraph.

Quantitative comparison (Table I) of the observed and calculated s values $\left(s = \frac{4\pi}{\lambda} \sin \theta/2\right)$ also shows that the best agreement is for the 92.5° model with C-C single-bond distance 1.55 Å. and C-C double-bond distance 1.34 Å. The 90° model with C—C single-bond distance 1.55 Å. and -C double-bond distance 1.30 Å. shows a larger Caverage deviation. As discussed above this curve is also considered less satisfactory on the basis of qualitative agreement with the appearance of the observed pattern. The final results are C-C = 1.55 ± 0.02 Å., C=C = 1.34 ± 0.03 Å., and $\angle C_4C_1C_2 = 92.5^\circ \pm 2^\circ$, in fair agreement with Bauer and Beach, who reported $C - C = 1.56 \pm$ 0.03 Å., C=C = 1.34 ± 0.02 A., and $\angle C_4C_1C_2 =$ 90°.

-12-

In spite of the exclusion of the spiropentane model by the radial distribution curve, a theoretical intensity curve shown in Fig. 1 was calculated for the spiropentane model of Rogowski³ for the full s_0 range of our pictures. This curve is in essentially complete disagreement with the observed diffraction pattern, although the positions of the main features are similar.⁴

1-Methylcyclobutene.—The appearance of the diffraction pattern is generally similar to that observed for methylenecyclobutane, but shows numerous distinct points of difference. For 1methylcyclobutene the first maximum is broader, and higher on the inner side; the shelf-like fourth maximum is less distinctly separated from the third; the fifth minimum is broader and the fifth maximum rises more gradually on the inner side. The sixth maximum is stronger and sharper, and the seventh maximum shows structure on the outer side, which is not too clearly distinguishable. The stronger peaks of the radial distribution curve marked RD in Fig. 2 are at 1.09, 1.54, 2.16 and 2.72 Å. The double-bond distance is not resolved. It was varied from 1.30 to 1.38 Å. in calculating the theoretical intensity curves.

Since the double bond is in the ring in 1-methylcyclobutene there is no doubt that the carbon atoms are coplanar. The same assumptions regarding the hydrogen atoms were made as above. The C-C single-bond distance was taken from the radial distribution curve to be 1.54 Å. The angle $C_5C_1C_2$ was varied from 110 to 140°. About 25 theoretical curves were calculated, of which representative examples are shown in Fig. 2. Curves A to G have double-bond distance 1.34 Å. and the $\angle C_5C_1C_2$ indicated; curves H and I have double-bond distances 1.30 and 1.38 Å., respectively, with $\angle C_5C_1C_2 = 125^\circ$. In all except curves F and G the ring structure was made symmetrical ($\angle C_2C_3C_4 = \angle C_1C_2C_3$; $\angle C_3C_4C_1$ = $\angle C_4C_1C_2$). For curve F the ring was distorted by increasing the $\angle C_4C_1C_2$ by 5°, and in curve G by decreasing the same angle 5°, changes in other angles being made symmetrically but retaining the same external $\angle C_5C_1C_2$ (= 125° in these curves). On the basis of the features of the observed pattern described above, best agreement was found for the symmetrical ring with doublebond distance 1.34 Å. and 120° < angle $C_{b}C_{1}C_{2}$ < 130°.17 Curve C (125°) was chosen as best, with calculated non-bonded $C \cdots C$ distances 2.11, 2.71, 2.74 and 3.63 Å. The most important $C \cdots H$ terms are in the neighborhood of 2.20 Å.



Fig. 2.

These distances with their relative weights are shown on the curve RD of Fig. 2. Quantitative comparison of observed and calculated *s* values for Curve C (125°) is made in Table II. Our final results are C—C = 1.54 ± 0.03 Å., C—C = 1.34 ± 0.03 Å., $\angle C_5C_1C_2 = 125^\circ \pm 4^\circ$, $\angle C_4C_1C_2$ = $93^\circ 40' \pm 3^\circ$, etc. (*i. e.*, symmetrical ring structure $\pm 3^\circ$ distortion).

TADIET

				I MODE I		
			METHYLI	ENECYCLOB	UTANE	
Max.	Min.	<i>S</i> 0	se (92.5°) 1.34	sc/so	se (90°) 1.30	sc/s0
	1	4.14	3.61	(0.872)	2.82	(0.688)
1		5.89	5.90	(1.000)	6.06	(1.030)
	2	7.42	7.78	1.048	7.92	1.067
2		9.44	9.35	0.990	9.27	0.982
	3	10.84	11.00	1.014	10.81	1.017
3		12.66	12.66	1.000	12.63	0.998
	4	13.80	14.04	1.017	13.95	1.011
4		14.76	14.83	1.004	14.89	1,009
	5	16.18	16.05	0.992	16.02	0.990
5		17.70	17.36	.980	17.47	.987
	6	19.36	19.10	.987	19.07	.985
6		21.32	21.33	1.000	20.67	.969
	7	23.05	23.03	0.999	22.70	.984
7		24.93	24.91	.999	25.37	1.017
8		29.30	29.31	1.000	29.30	1.000
				1.002 =		1.002 =
				0.011		0.019

Discussion.—Although the diffraction data for the two substances considered here can be interpreted satisfactorily on the basis of planar cyclic models in agreement with the chemical identification of these substances as methylene-

⁽¹⁷⁾ The $C_5 \cdots C_2$ and $C_5 \cdots C_3$ distances and their associated $C \cdots H$ terms, which together are the most important in determining the structure-sensitive features of the theoretical curves, are equal at about $\angle C_5 C_1 C_2 = 125^\circ$. Consequently a considerable variation of this angle in either direction produces only relatively small differences in the resulting curves, and prevents a close determination of the angle. Similarly curves calculated for distortions of 2 and 5° of the ring in either direction in the manner described above show that distortion of about 5° in either direction is required to produce definite disagreement for the best curve, and does not improve agreement for the other curves.

W. SHAND, JR., VERNER SCHOMAKER AND J. RODNEY FISCHER

		TA	BLE II				
1-METHYLCYCLOBUTENE							
Max.	Min.	S0 .	Sc	se/so			
	1	4.09	3.30	(0.807)			
1		5.81	5.97	(1.027)			
	2	7.89	8.01	1.014			
2		9.43	9.38	0.995			
	3	11.00	11.00	1.000			
3		12.57	12.57	1.000			
	4	13.39	13.57	1.013			
4		14.46	14.29	0.989			
	5	15.51	15.47	.998			
5		17.89	17.84	.998			
	6	19.78	19.95	1.008			
6		21.49	21.21	0.987			
	7	22.97	22.70	.989			
7		24.95	24.91	.998			
	8	27.51	27.39	.996			
8		29.52	29.85	1.009			

 0.999 ± 0.006

cyclobutane and 1-methylcyclobutene, it is clear from the similarity of the photographs that a unique identification by means of electron diffraction alone would be difficult, and, from a comparison of the theoretical curves, impossible. This is shown by the practical identity of curve 92.5° of Fig. 1, the best methylenecyclobutane curve, with the 1-methylcyclobutene curves B (120°) and C (125°) of Fig. 2.18 This is to be expected for molecules whose scattering distances $(r_{ij}s)$ differ only in what amounts to second order effects: about 70% of the scattering (based on the weight of the coefficients $Z_i Z_j / r_{ij}$) is due to rij's identical for the two models and the remainder is due to r_{ij} 's which are not markedly different. It should be emphasized again that the attempt to differentiate between different chemical structures by the electron diffraction method may not always lead to a unique result, especially when a reasonably great variation of the models representing the various chemical structures is allowed. Where the proposed structures are, however, fundamentally different in geometrical design, the corresponding sets of interatomic distances are usually quite different and a definite choice is made possible.¹⁹ Thus the comparison of the theoretical curves and the diffraction photographs provides definite detailed evidence that neither of our substances is spiropentane.

(18) The similarity of the theoretical curves was overlooked by Bauer and Beach⁴ because an error in the cross-ring distance was made in the calculation of their curves E for 1-methylcyclobutene and F for 3-methylcyclobutene. Their model E (private communication from Professor Bauer) was nearly the same as our D (130°).

(19) See for example R. A. Spurr and V. Schomaker, *loc. cil.*; J. Waser and V. Schomaker, THIS JOURNAL, **65**, 1451 (1943).

Moreover, a preliminary comparison of the radial distribution curves with the distances to be expected for the models in question at once makes improbable all of the other isomers which contain no four-membered ring, mainly because none of these would give a strong peak at about 2.2 Å. but only a C...H peak, while suggesting the possibility that for 3-methylcyclobutene a reasonable model leading to intensity curves in agreement with the photographs (especially of 1-methylcyclobutene) could be found. It was not thought profitable, however, further to consider these various structures inasmuch as there seemed to be no doubt about the chemical identification and it seemed likely that even after careful consideration by the correlation procedure not all of them could be ruled out with certainty.

The question of the distribution of "strain" in these molecules is of interest. In methylenecyclobutane the strain in the four-membered ring can be taken up by expanding the H-C-H angle to compensate for the compression of the -C--C angle at the C₂, C₃ and C₄ positions; at C₁ such compensation cannot occur except by increase of the angle $C_4C_1C_2$, as observed. In 1methylcyclobutene a symmetrical ring structure would be expected if the C_5C_1 single bond were sterically equivalent to the C-H single bond. The angle $\hat{C}_5C_1C_2$ which distributes equally the distortions from the normal values of the bond angles about the C₁ carbon atom is 125°, in agreement with the angle $125 \pm 4^{\circ}$ found above. The angle distortion for the system C--C-C is then nearly equal to that for C--C, indicating that in this case at least the effective bending constants for the two systems are apparently not markedly different.

The results of Rogowski³ are not clarified. A radial distribution analysis of his s_0 values leads to the distances 1.55 and 2.88 Å., in agreement with the spiropentane model. In the absence of more details on the preparation and physical constants of the substance used in his investigation no further explanation can be given than was offered by Bauer and Beach.

The authors wish to express their thanks to Dr. E. R. Buchman for suggesting this research, and for his assistance and interest in the work.

Summary

The preparation and physical constants of methylenecyclobutane and 1-methylcyclobutene are described. The electron diffraction investigation of these compounds shows that they are cyclic structures with the expected configurations and distances.

PASADENA 4, CALIFORNIA RECEIVED NOVEMBER 3, 1943

The Molecular Structures of some Heterocyclic Compounds.

Of the simple saturated heterocyclic compounds only ethylene oxide (13, 14), dioxane-1,4 (15), and paraldehyde (13, 16) have been investigated by the electron diffraction method. In this Section are given the results of a reinvestigation of the structure of dioxane-1,4, and of the structural determinations by the electron diffraction method of the heterocyclic compounds trimethylene oxide, ethylene methylene dioxide, trioxane-1,3,5, pyrazolidine, and 1,2-trimethylenepyrazolidine. Throughout this investigation the author has been fully aware of the difficulties inherent in the determination of the structures of planar (or nearly planar) five- and six-ring molecules by means of the electron diffraction method.

The difficulties arise from the fact that the geometry of the planar five- and six-rings is such that unattainably great precision in the determination of the various interatomic distances is required in order to fix the parameters defining the structures within usefully small limits. It would be necessary to measure separately individual interatomic distances which are so closely similar, for example, as to be unresolved by the radial distribution function, or to determine with extreme accuracy the averages of such unresolved groups of interatomic distances. It is even possible in most cases of distances not greatly dissimilar (such as C-C and C-O, or C-C and C-N) to interchange the values of the bond lengths before producing disagreement of the theoretical curves, so that a very large range of individual bond distances is permissible. Average distances are, however, generally nearly invariant to such variations.

-14-

Therefore the information given by the radial distribution function can be reproduced by a rather wide range of individual interatomic distances and bond angles, and accordingly acceptable theoretical intensity curves can be drawn for the same wide range of parameters. This is borne out by the fact that the diffraction patterns of planar five-ring (or six-ring) organic molecules of roughly similar structure do not vary in appearance to any great extent (aside from scale factor), as shown by this work, and that of Schomaker and Pauling (17) on furan, pyrrole, and cyclopentadiene on one hand, and benzene, pyridine, and pyrazine on the other. Hence precise determinations of all the structural parameters in the series of molecules under investigation are not feasible.

Experimental. The trimethylene oxide, b.p. 47.2° C (760 mm), was prepared from **y**-chlorpropylalcohol (18) by Mr. A. Reims in these Laboratories. The ethylene methylene dioxide, b.p. 74° C (745 mm) was prepared by the method of Verley (19). The dioxane, b.p. 100° (745 mm) was a specially purified fraction of dioxane obtained from the chemical stockroom. The trioxane, m.p. $61-62^{\circ}$ C, b.p. 114° C (760 mm), was obtained from Mr. P. J. Carlisle of the E. I. duPont de Nemours Electrochemicals Dept. The samples of pyrazolidine and 1,2-trimethylenepyrazolidine (20) were obtained from Prof. Wiselogle of Johns Hopkins University.

All photographs, with the exception of those of trimethylene oxide, which were made at room temperature, were made at $70-150^{\circ}$ C with the high-temperature nozzle described by Brockway and Palmer (21). The

-15-

wavelength of the electrons, determined either from transmission photographs of gold foil or zinc oxide smoke (11), was about 0.061 Å., and the camera distance was about 10.9 cm. Some photographs of trimethylenepyrazolidine were made with a camera distance of 20.25 cm. Corrections were made for film expansion. In all calculations the C-H bond length was assumed to be 1.09 Å. The plane of the H-C-H angle was taken perpendicular to the plane of the angle formed by the carbon atom of the methylene group and the two adjacent ring atoms. Each of these angles was bisected by the plane of the other. The value of the H-C-H angle was determined by distributing the deviation of the X-C-Y angle from the tetrahedral value among the other valence angles of the carbon atom. Analogous assumptions were made regarding the N-H terms, for which the bond length 1.02 Å. was assumed. The temperature factor a_{i,j} was taken to be 0.00015 for bonded hydrogen terms, 0.00030-0.00045 for non-bonded hydrogen terms, and zero for all others. Particular attention was given features beyond q = 50, since because of the effect of the temperature factor, the outer rings are not especially sensitive to special assumptions made regarding the hydrogen atoms.

(a) <u>Trimethylene oxide</u>. The visual appearance of the photographs is shown in the curve marked V in Fig. 1. The radial distribution curve, marked RD, shows strong peaks at 1.10 $\stackrel{\circ}{\text{A}}$. (C-H), 1.48 $\stackrel{\circ}{\text{A}}$. (average of C-C and C-O), and 2.15 $\stackrel{\circ}{\text{A}}$. (average of C···C and C···O, and H···X; $\sim \sqrt{2} \ge 1.48 \stackrel{\circ}{\text{A}} = 2.09 \stackrel{\circ}{\text{A}}$., in agreement with a planar cyclic model).

The determination of the shape of this molecule mainly concerns the two larger (unresolved) peaks of the radial distribution, and in

-16-

particular the important points in question are the ratio of the averages of the distances represented by the two peaks, and the differences of their widths. The correlation procedure might be expected to give somewhat more information regarding the precise distribution of the terms within each peak through the related appearance of the outermost features of the theoretical intensity curves. The appearance of the inner features is affected by the necessary assumption of the positions of $H^{\bullet,\bullet,\bullet}X$ terms, which, however, have strong temperature factors. It will thus be true that information which might be gained by a detailed analysis would be subject in some degree to the accuracy of these assumptions. Theoretical intensity curves were calculated for both planar and non-planar models with the configuration $C_{T_{eq}}$



with the simplifying assumption that $\angle OC_1C_2 = \angle C_1C_2C_3 = \angle C_2C_3O = \mathbf{\beta}$. With this assumption both $\boldsymbol{\alpha}$ ($\angle C_1OC_3$) and $\boldsymbol{\beta}$ are determined by the ratio C-O/C-C for planar models. The H-C-H angle was taken to be about 116°, with the assumptions regarding the hydrogen terms mentioned in the previous section. Curves A to E, Fig. 1 were calculated with C-C = 1.54 Å. and C-O = 1.40 to 1.53 Å. at intervals of 0.03 Å. As can be seen by reference to Fig. 1, best qualitative agreement for coplanar models is found for C-O = 1.46 Å. (Curve C). For this model $\boldsymbol{\beta} = 88.5^{\circ}$ and $\boldsymbol{\alpha} = 94.5^{\circ}$. Some planar models (Curves F, B, and H) were also calculated in which the restriction $\angle OCC = \angle CCC$ was removed. In these models $\angle C_1C_2C_3$ was taken to be 90° and $\boldsymbol{\alpha}$ varied from 92°-97°. Agreement with the visual curve was not satisfactory until the C-C distance was made nearly equal to the C-O distance, and was not very good in any case. The planarity of the structure was investigated briefly by moving C_2 out of the plane of C_1OC_3 , and varying Θ , the angle between the planes of $C_1C_2C_3$ and C_1OC_3 , from 10° to 40° . These curves were unsatisfactory in that the asymmetry of the first and third peaks became wrong, and the region of the sixth and seventh maxima did not agree with the observed pattern. Curves I and J are for $\Theta = 25^\circ$ and $\Theta = 17^\circ$ respectively. The trend of the non-coplanar curves indicated that a deviation from planarity by more than about $25 - 30^\circ$ would be required to give theoretical curves inconsistent with the observed pattern.

Comparison of observed and calculated q values (Table I) leads to the distances $C-0 = 1.46 \pm 0.03$ Å.; $C-C = 1.54 \pm 0.03$ Å., and the angles $\beta = \angle C-C-C = \angle C-C-0 = 88.5^{\circ} \pm 3^{\circ}$ and $\alpha = \angle C-0-C = 94.5^{\circ} \pm 3^{\circ}$. The molecule is probably planar within $15 - 20^{\circ}$.

Table I

TRIMETHYLENE OXIDE

Max	Min	q <u>obs</u>	q _{calc} (C)	q _c /q _o (C)
	1	8.51	8.50	(0.999)
1		12.30	12.00	(0.976)
•	2	16.35	16.75	(1.025)
5	7	20,21	20.25	1.002
z	2	29.20	25.00	0.992
)	4	35.50	35-40	0.997
4		41.09	41.80	1.017
	5	43.27	45.00	(1.040)
5		46.29	48.00	(1.037)
~	6	52.40	52.20	0.996
6	7	57.82	57.60	0.996
7	1	60 67	63. (U	0.999
1	8	75.43	75-30	0.998
g	U U	80.32	80.00	(0.996)
	9		- not measured -	())-/
9		84.94	85.20	1.003
	10	90.11	90.80	1.008
10		94.60	96.90	(1.024)
			Average	1.001
			Average Deviation	0,005



Figure 1

Trimethylene Oxide

Legend for Figure 1

Trimethylene Oxide.

V	Visual Curve.					
RD	Radial Distril	oution Cur	ve			
	C-0 Å.	c-c 2.	ø	P	p'	θ
A B C D E F G H I J	1.40 1.43 1.46 1.49 1.52 1.43 1.43 1.43 1.43 1.43	1.54 1.54 1.54 1.54 1.54 1.45 1.45 1.54 1.54	98 ⁰ 36 96 30 94 36 92 54 91 6 91 30 94 10 96 40 93 96	87 ⁰ 81 87 50 88 28 89 2 89 38 89 15 87 55 86 40 87 87	87 ⁰ 81 87 50 88 28 89 2 89 38 90 90 87 87 87	0° 0 0 0 0 25°20' 16 45

.

(b) Ethylene Methylene Dioxide. The visual appearance of the photographs is shown by the curve V of Fig. 2. The shelf on the visual curve at about $q \approx 55$ was incorrectly drawn too prominently, as was evident upon re-examination of the photographs. The radial distribution curve marked HD shows strong peaks at 1.43 Å. and 2.31 Å., with C-H peaks at 1.12 Å. and 3.18 Å. If the C-C bond length is assumed to be 1.54 Å., the weighted average bond length 1.43 Å. from the radial distribution curve gives a C-O bond length of 1.415 Å. The distance 2.31 Å., which corresponds to a weighted average of the five cross-ring distances, leads to an average angle of about 108°, in good agreement with a planar pentagonal model. Theoretical intensity curves were calculated for pentagonal models with the configuration



with the matio C-O/C-C varied from 1.38/1.54 to 1.46/1.54, corresponding for planar models to a variation of \propto from 95° to 112°, of pfrom 101° to 118°, and of γ from 101° to 107°. The theoretical curves are relatively insensitive to parameter changes for the reasons mentioned above in this section, and, moreover, it turns out that in this case no more information can be obtained from the correlation procedure than is given by the radial distribution curve. A curve calculated for a non-planar model, with the angle of the plane of 0-C-O inclined at 20° to the plane of 0-C-C-O cannot be distinguished from the curve for the best planar model; a deviation of about 40° to 50° is

-22-

required before definite disagreement is observed. Agreement can also be obtained by assuming two different C-O bond lengths (b = 1.38 Å., and b' = 1.46 Å., for example, Curve E of Fig. 2), although small points of difference begin to appear. The C-O bond length reported here must accordingly be interpreted as an average of the four bonded carbon-oxygen distances. It is thus seen that there is a rather large range of variation of the structural parameters within which qualitative good agreement with the observed pattern can be obtained. Quantitative comparison of observed and calculated q values for model B is given in Table II. With the assumption that b = b', i.e. that all the C-O bond lengths are the same, the final results are: $C-O_{Av.} = 1.42 \pm 0.03$ Å., $C-C = 1.54 \pm 0.05$ Å. No limits on the variation of the individual angles can be given, although it seems likely none of them deviate widely from 108° .





Figure 2

Legend for Figure 2

Ethylene Methylene Dioxide

•

v	Visual	Curve					
RD	Radial	Distributio	on Curve c-c	ø	ß	۲	ອ
A		1.46	1.54	108 ¹⁰	109 ⁰ 111	106 341	൦ഁ
в		1.42	1.54	1081	110 9	105 36	0
C		1.38	1.54	108 1	111 4	104 41	0
D		1.42	1.54	109 52'	106 36	106 6	17°51'
Е		1.46 1.38	1.54	109	111 45	103 45	0

•

Table II

Max	Min	qobs	q (B) calc	q _c /q _c (B)
1	1	7.03 10.87	7•55	(1.074)
_	2	14.60	14.00	(0.959)
2	7	19.06	19.60	1.028
3	د	23.95	24.50	1.019
)	4	32.53	32.80	(1.008)
4	_	36.66	35.40	(0.965)
5	5	40.61 115.33	39•50	0.973
)	6	49.85	50.45	1.012
6		54.35	54.60	(1.005)
7	7	58.09	56.65	(0.975)
1	8	66.65	66.55	0.914
g		72.06	72.00	0.999
0	9	77-37	75.40	(0.975)
9	10	83.52	82.75	0.991
10		87.88	88.00	1.001
			Average	1.001
			Average Deviation	0.014

ETHYLENE METHYLENE DIOXIDE

•

(c) <u>Dioxane-1,4</u>. The photographs showed eleven features compared to the four reported by Sutton and Brockway (15). The visual appearance of the photographs is shown by the curve V of Fig. 3. The radial distribution curve marked RD has strong peaks at 1.46 Å., 2.40 Å. $(= 2 \times 1.46 \sin 111^{\circ}/2)$ and 2.78 Å., in agreement with a puckered six-ring structure. In calculating the theoretical intensity curves it was assumed that the molecule had the "chair" (or "Z") form as indicated by the observed zero dipole moment, with the configuration



(One oxygen atom is above, and one below the plane of the paper). Only hydrogen-oxygen and hydrogen-carbon interactions of atoms separated by not more than one other atom were included, with the usual assumptions regarding the temperature factor, since it was found that the inclusion of longer terms than these, with appropriate temperature factors, did not alter the appearance of the several preliminary curves. The ratio C-O/C-C was varied from 0.93 to 1.0 and the angles $\alpha = / C-O-C$ and $\beta = / C-C-O$ were varied from 106° to 117° . As can be seen by reference to the theoretical intensity curves of the figure best agreement was found for models with an average angle of about 1102° , with a difference between / C-O-C and / C-C-O of about 3° , corresponding approximately to $/ C-O-C = 1122^{1^{\circ}}$, and $/ C-C-O = 1092^{\circ}$. The allowable variation of the average angle for ratios of C-O/C-C between

-27-



Figure 3 Dioxane-1,4

Legend for Figure 3

Dioxane-1,4

,

RD	Radial	Distril	oution	Curve	9
٧	Visual	Curve			
	C-	-0	C-C	(×

	C-0	C-C	Ø	ß
A	1.43	1.54	112°	109°30'
в	1.44	1.51	113 401	111 20
C	tt	ที่	108	109 30
D	11	11	110	109 30
Ε	н	"	112	109 30
F	н	11	114 30	109 30
G	11	88	109 10	106 40
H	1.46	1.51	113 40	111 20
I	11	#	116 20	111 20
J	18	11	112	1093
K	11	10	114 30	109 30
L	5_ 11	11	117 20	109 20
M	11	11	112 20	107 20
N	1.48	1.51	115 40	111 40
0	11	11	112	111 15
P	11	H	112	109 30
Q	H	н	113 35	108 35
R	~ H	11	110 30	108
S	1.51	1.51	112	109 30

Table III

DIOXANE-1,4

Max	Min	′ q _o	$q_{c}/q_{o}(D)$	$q_c/q_o(E)$	q _c /q ₀ (J)	$q_{c}/q_{0}(P)$
l	1	6.14 9.51	(1.181) (1.056)	(1.181) (1.052)	(1.180) (1.052)	(1.148) (1.052)
~	2	13.42	(0.991)	(1.002)	(0.976)	(0.969)
2	3	23.70	1.012	1.018	1.004	0.993
3	,	29.58	1.004	1.006	0.997	0.980
4	4	32.67 36.06	(1.025) (0.996)	(1.016) (0.998)	(1.032) (0.990)	(1.022) (0.978)
	5	40.12	0.975	0.977	0.960	0.952
5	6	44.08 48.12	1.000 1.016	0.998 1.018	0.985 0.999	0.979 0.998
6	_	51.96	1.004	1.001	0.985	0.983
7	7	55.61 60.07	0.989	0.990	0.980	0.973
1	8	64.51	1.000	1.000	0.982	1.000
8		68.91	1.023	1.010	1.004	0.998
•	9	71.87	(1.033)	(1.021)	(1.009)	(1.016)
9	10	(5.60 80.15	(1.019)	(1.011)	(1.000)	(1.007)
10	10	85.00	1.012	1.012	1.000	0.989
	11	91.47	0.993	0.992	0.982	0.976
11		96.64	0.978	0.978	0.970	0.963
	Average		1.002	1.001	0.990	0.983
	Average	Deviation	0.01]	0.012	0.011	0.013
	C-C		1.51	1,51	1.49	1.484
	C-0		1.44	1.44	1.445	1.45 ₅

. . . .

0.94 and 0.98 was about $\pm 2^{\circ}$, while the variation in the individual values of the angles was about 10°. The range of variation of the parameter C-O/C-C within which acceptable theoretical curves were found was from about 0.94 to 0.98. A sufficient number of theoretical curves was calculated (not all of those calculated are shown in Figure 3) so that it was possible to be sure by short range interpolation or extrapolation that agreement was definitely worse in all directions in parameter space from the best models. The most satisfactory model is that for curve E, which best reproduced all the features of the photographs. Quantitative comparison of observed and calculated q values for models D, E, J, and P are given in Table III. The final results are $C-0 = 1.44 \pm 0.03$, $C-C = 1.51 \pm 0.04$, $/ 0-C-C = 109\frac{1}{2}^{\circ} \pm 5^{\circ}$, / C-O-C = $112^{\circ} \pm 5^{\circ}$. The average angle is determined much more closely to be $110\frac{1}{2}^{\circ} \pm 2^{\circ}$. These distances are somewhat smaller than those found by Sutton and Brockway (15), who reported $C-0 = 1.46 \pm 0.04 \text{ Å}$. C-C = 1.56 Å. (assumed), $\angle C-O-C = 110^{\circ} \pm 5^{\circ}$, and $\angle C-C-O = 109^{\circ}28^{\circ}$ (assumed). The present results are believed to be the more reliable because of the considerably greater amount of information afforded by the new photographs.

(d) Trioxane (X - Trioxymethylene). The visual appearance of the photographs is shown by curve V of Fig. 4. The observed pattern is guite similar to that of dioxane-1,4. The radial distribution curve marked RD has peaks at 1.13 Å. (C-H), 1.40 Å. (C-O), 2.06 Å. $(C \cdot \cdot H, O \cdot \cdot H)$, 2.32 Å. $(O \cdot \cdot \cdot O, C \cdot \cdot \cdot O = 2 \times 1.405 \text{ sin } 111^{\circ}/2)$, and 2.73 Å. (C···O), indicating a puckered ring structure. The planar ring structure can be eliminated since one would then expect distances $\sqrt{3}$ x 1.41 Å = 2.44 Å, and at 2 x 1.41 Å = 2.82 Å. The theoretical int ensity curves for the "chair" and "tub" forms of the molecule are practically indistinguishable, and most of the calculations were made only for the "chair" form. All angles in the ring were assumed to be equal (/ C-O-C = / O-C-O) and all C-O bond distances equal. Curves were calculated for angles 106°, 109.5°, 112°, 115°, and 120° (planar form), with C-O bond length 1.41 Å. Of these the curve for angle 112 best reproduced the observed pattern. Agreement is seen to be good. The discrepancy at the fourth ring between curves V and 112° arises because of what now seems to be an error in V. Agreement was not improved by making the angle C-O-C different from the angle 0-C-0 while keeping the average constant at 112, and was definitely made worse when the difference exceeded about 6. Quantitative comparison of observed and calculated q values (Table IV) shows that for the 112 curve the C-O bond length is 1.40 Å. C. F.

-32-

Moerman (22) has shown in an x-ray investigation that trioxane in the crystal has the symmetry C_{3V} ("chair" form). He gives the results $C-0 = 1.42 \pm 0.03$ Å., and $\angle C-0-C = 105^{\circ} \pm 10^{\circ}$.

The final results of this investigation are $C-0 = 1.40 \pm 0.02$ Å., and $\angle C-O-C = \angle O-C-0 = 112^{\circ} \pm 3^{\circ}$.
TABLE IV

TRIOXANE-1,3,5 (d-TRIOXYMETHYLENE)

Max	Min	q _{obs}	q _{calc} (112 [°])	q _c /q ₀ (112 [°])
	l	7.19	7.25	(1.008)
1	-	10.30	10.55	(1.024)
•	2	14.39	13.80	(0.959)
2	3	25.24	18.50	0.988
3	2	30.18	31.00	1.027
-	4	34.09	34.75	(1.019)
4		37.27	37.25	(0.999)
22.05	5	41.50	40.75	0.982
5	C	45.48	45.30	0.996
6	Ь	49.85	50.15	1.006
0	7	57-50	55.50	1.000
7	1	61.49	61.10	0.994
•	8	66.90	66.50	0.995
8		72.72	72.75	1.000
	9	75.64	76.00	(1.005)
9	10	78.40	78.00	(0.995)
10	10	03.05 88 88	83.45	1.005
10	11	94.29	93.50	0.997
11		100.02	97.25	(0.971)
	12	104.89	99.95	(0.953)

Average

0.995 ± 0.007



Figure 4 Trioxane

-35-

Legend for Figure 4

Trioxane-1, 3, 5

V Visual Curve

.

RD Radial Distribution Curve

For all curves C-O is equal to 1.41 Å., and \angle C-O-C has the value indicated with each curve.

(e) <u>Pyrazolidine</u>. The visual appearance of the photographs is shown by curve V of Fig. 5. The radial distribution curve marked RD has strong peaks at 1.48 Å. and 2.38 Å. (= 2 x 1.48 sin $107^{\circ}/2$), with C-H and N-H peaks at 1.06, 2.12, 2.95, and 3.08 Å. For a regular pentagon the ratio of diagonal to side is 1.618, while 2.38/1.48 = 1.609. For pyrazolidine the symmetrical configuration



was assumed. The ring was assumed to be coplanar, since it was found that one atom could be displaced so that the angle of the plane formed by it and its adjacent atoms with the plane of the other atoms had to be varied up to about 40° before causing appreciable disagreement with the planar model having the same bond lengths. The assumption was made throughout that the C-N bond length is equal to the N-N bond length.

For this type of structure, as discussed above, there is a wide range of variation of parameters within which agreement can be obtained. For a particular value of the ratio C-N/C-C, the variation of angles of the ring is about $108^{\circ} \pm 4^{\circ}$, as shown by the series of curves A, D, E, F for the ratio C-N/C-C = 1.47/1.54. For other values of this ratio a similar range of angle values will doubtless be found. For various values of the ratio C-N/C-C, the size of the molecule was determined by comparison of observed and calculated q values. This comparison is shown in Table V for the ratios C-N/C-C given values 1.47/1.54, 1.47/1.51, and 1.47/1.48, corresponding to the curves B, C, and D respectively. Since these curves are all satisfactory it is not possible to set an interestingly small upper limit on the C-N bond length, as increasing C-N further corresponds to exchanging the C-C and C-N bond lengths and reversing the series. In the direction of a lower limit, however, the increased splitting of the bond distances will rapidly lead to disagreement. It is seen that the average bond distance for the best models is roughly invariant and about 1.48 Å., confirming the information given by the radial distribution curve. For various values of the C-C distance, the average C-N and N-H distances are given in Table V. For model C, which gives the normal C-N and N-N bond length 1.47 Å., the C-C bond length is 1.51 Å., with angles \angle N-N-C = 109°, \angle N-C-C = 107½°, \angle C-C-C = 107°.

TABLE V

PYRAZOLIDINE

Max	Min	₫ ₀	q _c /q _c (B)	q _c /q _c (C)	q _c /q _o (D)
1	l	7.15 10.56	(1.007) (0.956)	(1.035) (0.956)	(1.049) (0.966)
2	2	14.64	(0.871)	(0.854)	(0.837)
~	3	24.05	0.986	0.994	1.009
3	(4)	28.54 31.26	0.988 (1.001)	0.991 (1.008)	0.999 (1.011)
(4)	(5)	34.86 38.73	(0.990)	(0.975)	(0.970)
5	6	43.93	0.979	0.988	0.992
(6)		53.50	(0.982)	(0.982)	(0.991)
7	(7)	56.26 59.08	(0.973) 0.999	(0.978) 1.002	(0.990) 1.009
g	g	64.24 69.35	0.999	1.004	1.012
0	9	73.57	0.999	1.006	1.017
9	10	79.46	1.000 \	1.003	1.008
10	11	83.44 89.54	1.007 0.999	1.016	1.023 1.014
11		94.89	0.995	1.007	1.014
Avera Avera	ge ge Devi	iation	0.996 0.006	1.002 0.005	1.009 0.006
C-C N-N,	C-N		1.53 1.46	1.51 1.47	1.49 1.48

.



Pyrazoli**di**ne

Legend for Figure 5

Pyrazolidine

- V Visual Curve
- RD Radial Distribution Curve

	C-N N-N	c_c	¢	ß	r
A	1.47	1.54	106°	116°14'	95°321
в	11	1.48	108 30	107 15	108 30
С	11	1.51	109	107 30	107
D	H	1.54	109 30	107 45	105 30
Ξ	11	1.54	110 35	104 26	108 58
F	H	1.54	112	101 24	113 12

.

(f) <u>1,2-Trimethylenepyrazolidine</u>. The visual appearance of the photographs, shown in curve V of Fig. 6, is similar to that observed for pyrazolidine, as is to be expected. The radial distribution curve, marked RD, has strong peaks at 1.49 Å. and 2.40 Å., with minor peaks at 2.13 Å., 2.88 Å., 3.12 Å., 3.46 Å., and 3.70 Å. Good resolution of the longer distances, which contribute only about 20% of the scattering, was not obtained. The first strong peak includes the C-C, C-N, and N-N bond distances; the second is due to the intra-ring diagonal distances as well as two of the inter-ring distances. The peaks at 2.13 Å. and 3.12 Å. are C···H peaks.

In calculating the theoretical intensity curves the pyrazolidine curves were used as a guide, since the trimethylenepyrazolidine curve is essentially that for two pyrazolidine rings plus a few inter-ring distances which do not greatly alter the fundamental pattern. The configuration (including planarity) and distances described above for the pyrazolidine ring were assumed, and the angle 9 between the normals to the planes of the two pyrazolidine rings was varied. Curves were calculated for $\theta = 0^{\circ}$ (planar model, $\epsilon = (C_N - C' = 142^{\circ}), \theta = 58^{\circ}40'$ $(\epsilon = 111^{\circ})$, and $\theta = 83^{\circ}10^{\circ}$ ($\epsilon = 90^{\circ}$). A curve was also calculated for a planar model ($9 \approx 180^{\circ}$) in which the rings were compressed to give the same long C···C distances as in the model for $\theta = 58^{\circ}40^{\circ}$. The compressed planar model does not give qualitative agreement with the observed pattern. Of the first three models, that with $\theta = 58^{\circ}40^{\circ}$ (curve B, Fig. 6) gives the best qualitative agreement with the visual curve. The latter model also explains best the 3.46 Å. peak of the

-42-

radial distribution curve, none of the other models having distances near this value. Quantitative comparison of observed and calculated q values also shows (Table VI) that a curve near model B is satisfactory. The range of satisfactory models can be seen to be quite large; and it can only be said that models similar to B are satisfactory, that the shortest inter-ring heavy-atom distances are most probably at about 2.40 Å. (as in model B), and that the individual rings must have configurations close to that of pyrazolidine itself. If these rings were not held strictly planar a somewhat closer fit to the outer region of the radial distribution curve might be found (e.g. the peaks at 2.88 Å. and 3.70 Å), but this improvement would not necessarily be significant.

TABLE VI

1, 2-TRIMETHYLENEPYRAZOLIDINE

Max	Min	^q obs	^q calc	q_/q
1	_	5.38	5.80	(1.078)
	1	7.10	7•55	(1.063)
2		9.12	9-45	(1.036)
	2	10.65	12.60	(1.183)
3		14.72	15.20	1.032
	3	18.61	19.00	1.021
4		23.59	23.35	0.990
	4	27.89	28.45	1.020
5		31.42	32.70	1.040
	5	34.48	34.75	1.008
6		38.74	38.60	0.997
	6	43.58	42.90	0.985
7		48.60	49.25	1.013
	7	53.13	53.25	1.002
8		55.91	55.80	0.998
	ଞ	58.95	59.50	1.008
9		63.95	63.90	0.999
-	9	70.02	69.90	0.998
10		73.55	74.05	1.006
	10	76.96	76.95	1.000
11		81.31	80.25	0.999
	11	85.88	84.20	0.981
12		91.27	90.55	0.992
*	12	94.84	94.55	0.997
		Average		1,003
		Average	Deviation	0.010
				OF OTO



1.2-Trimethylenepyrazolidine

Legend for Figure 6

1,2-Trimethylenepyrazolidine

.

v	Visual curv	e			
RD	Radial Dist	ribution Curve			
A	a = 109 ¹ / ₂ °	β= 107 [°] 22'	1 = 106°16'	e = 142 [°]	$\theta = 0^{\circ}$
в	"	II	n	$\epsilon = 111^{\circ}$	0 = 58°401
C	II	11	H	E = 90 [°]	9 = 83°10'
D	∝ = 115 [°]	B = 1 06°5'	γ= 127°50'	e = 130 [°]	e = 0°

·		TABLE VII						
	0-0 0	C-X	х-х	0-x-0 7	x-2-2 7	D-D-0 7	C X-C-X	7 с-м-о
Trimethylene oxide	1.54± 0.03 Å.	1.46±0.03 Å.	1	94 8 4 3 °	88 31 30	୫୫ <mark>୫</mark> ୫3°	ı	1
Ethylene methylene dioxide	1.54±0.03 Å.	1.42±0.03 Å.	1	110°*	106°*	1	108° *	1
Di ozane-1, 4	1.51±0.03 Å.	1.44± 0.03 Å.	I	112°± 5°	109 1 5°	t	I	1
Tri oxane-1, 3, 5	× ţî	1.40±0.02 &	t	112 ± 3°	1	ł	112 ⁴ 5°	1
Pyrazolidine	1.51*	1°,47*	1°74	1		107° *	109° *	1
	Average bond	length 1.4840.05	8			,		
l, 2-Trimethylenepyrazolidine	Same distances	and angles assum	ned as in	pyrazolidi	ne			~111°
*Value given by best model.	Interestingly s	mell limits of v ³	eriation o	cannot be g	jven with	present da	te	

-47-

<u>Discussion</u>. The C-O, C-N, and C-C bond lengths found for the six molecules are summarized in Table VII. The distances found are all close to the normal values 1.43 Å. for C-O, 1.47 Å. for C-N, and 1.54 Å. for C-C. The bond angles are also close to those expected.

The C-O distance seems to show a definite trend in the following series of molecules: ethylene oxide 1.45 $\stackrel{\circ}{\text{A}}$. (13,14), trimethylene oxide 1.46 $\stackrel{\circ}{\text{A}}$, dioxane-1,4 1.44 $\stackrel{\circ}{\text{A}}$, ethylene methylene dioxide 1.42 $\stackrel{\circ}{\text{A}}$, and trioxane 1.40 $\stackrel{\circ}{\text{A}}$. For trioxane the shortening may arise from resonance of the normal structure with ionic structures of the following type:



This resonance would be analogous to that postulated by Brockway (23) to account for the observed shortening of the C-F bond in the fluoromethanes:



It might be expected that this type of shortening would be observed in other compounds with an O-C-O grouping, such as methylals, acetals, paraldehyde, metaldehyde, and similar compounds. As is pointed out in the following section these compounds actually have an anomalous heat of combustion amounting to about 19 kcal. per mole per 0-0-0 group. No appreciable shortening of C-O distance has been observed in paraldehyde and metaldehyde. For paraldehyde, which is 2,4,6trimethyltrioxane-1,3,5, Carpenter and Brockway (16) reported a distance of 1.43 \pm 0.02 Å. (Ackermann and Mayer (14) obtained agreement with an assumed value of 1.41 Å. in their investigation of this molecule.) In the ctystal of metaldehyde, which is the corresponding tetramer, Pauling and Carpenter (24) found a distance of 1.43 \pm 0.02 Å. No particular attempt, however, was made in either of these investigations to find whether better fits could be obtained for other values of the C-O bond length than the normal value 1.43 Å.

In dioxane-1,4 as well as in pyrazolidine the C-C bond length shows a rather low value. Although the magnitudes of the shortening are almost within the limits of experimental uncertainty in these cases, the effect is probably real. A similar shortening, presumably from the same effect, is found in diethyl ether, where the C-C distance has been found recently to be 1.50 ± 0.02 Å. (25). This effect has at present no satisfactory explanation.

The question of the planarity of the 1,2-trimethylenepyrazolidine bicycle is of interest in connection with attempts to resolve optical isomers of tervalent nitrogen (20,26). Although it was not possible to determine the angle between the planes of the two pyrazolidine rings to the usual degree of accuracy, the data indicate that the structure

-49-

is not planar. It follows therefore that optical isomers of substituted 1,2-trimethylenepyrazolidine may exist; but this possibility has not yet been borne out by resolution of such isomers.

<u>Summary</u>. The molecular structures of trimethylene oxide, ethylene methylene dioxide, dioxane-1,4, trioxane-1,3,5, pyrazolidine, and 1,2-trimethylenepyrazolidine have been investigated by the electron diffraction method. The results are summarized in Table VII.

The Molecular Structure of Ozone and Ozonides

(a) <u>Ozone</u>*. Although the cone molecule contains only three atoms, spectroscopic investigations have failed to give a detailed structure because of the difficulties of preparation, the great reactivity, and explosive nature of pure ozone. The present work was suggested by the idea that the purity of gas required for an electron diffraction determination is not so great as for spectroscopic work, and it seemed that a purity of 95% or better could readily be obtained in a suitable apparatus.

<u>Experimental</u>. The ozone was prepared by the method of Karrer and Wulf (27) using a silent electric discharge and an all-pyrex glass apparatus attached directly to a glass nozzle in the electron diffraction apparatus. A mixture of Apiezon M and graphite, which did not seem to be attacked by ozone, was used as a stopcock lubricant. Tank oxygen was passed through the ozonizer and a light blue mixture of oxygen and ozone

*With permission of the Editor, from J.Am. Chem. Soc. 65, 179 (1943)

-50-

was collected in a large trap cooled in liquid air. This mixture was fractionated into a smaller storage trap at hourly intervals until several ml. of blue-black ozone had accumulated for the final purification. This was fractionated into the large trap again and the system was pumpzed down until the pressure, at liquid air temperature, indicated by a Pirani gauge on the electron diffraction apparatus, was negligible. Enough ozone was usually made to fill a 300 ml. storage bulb at 1 atm. pressure.

It is important to establish the purity of the preparation. Oxygen (b.p. - 183° C.), nitric oxide (b.p. - 152° C.), and the other oxides of nitrogen (b.p. above 0° C.) boil at temperatures sufficiently removed from the boiling point of ozone (- 112° C.) that they should be nearly completely removed by the fractionation and pumping off of the residual gases. After each set of pictures the ozone was condensed in the traps and the pressure was always found to be of the order of a few mm., showing that little or no oxygen had been formed. (The v.p. of 0_3 at -180° C. is about 3 mm.). Deep blue ozone was observed in the traps of the electron diffraction apparatus after the exposures had been made, and the pictures obtained were uniform in appearance. Other investigators (27,28) using the same method of preparation have shown that pure ozone is obtained thereby.

The camera distance was ll.01 cm., and the wavelength of the electrons was 0.0615 Å. Five of the best pictures, showing four rings, were selected for interpretation.

-51-

Interpretation. Radial distribution curves were calculated by two methods according to the formula

 $rD(r) = \sum_{k} c_{k} \sin s_{k} r$ $C_{k} = I_{k}(s_{k}) e^{-\alpha s_{k}^{2}}$ $s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$ where $I_{k}(s_{k})$ is a visually estimated intensity assuming no falling off of intensity with s_{k} , and a is chosen so that $e^{-as_{max}} = 0.1$. The curve marked RDS of Fig. 7 was calculated using s_{k} values only at the maxima and minima of the observed curve; for the curve marked RDI, a plot of the visually estimated intensities was divided into about 40 segments, and the C_{k} 's estimated at each endpoint. The latter method is a good approximation to the integral inversion. Both methods give peaks corresponding to distances of 1.26 Å. and 2.24 Å., indicating an angle of 127°. The lines under the peaks show the distances finally chosen and their relative expected intensities.

Theoretical intensity curves, calculated using the simplified theoretical scattering formula

$I(s) = 2 Z_0^2 \frac{\sin 1.26s}{1.26} + Z_0^2 \frac{\sin l_{12}s}{l_{12}}$

for models having the form of an isoceles triangle with bond length 1.26 Å. and varying apical angle, are shown in Fig. 7. The characteristic features of the photographs, namely, the asymmetry of the second maximum, the depth of the third and fourth minima, and the complementary asymmetry of the third and fourth maxima, were best reproduced by the curve marked 127°. Table VIII gives the correlation of this curve with the measurements of the pictures.

Min	Max	s obs	scalc	s /s calc
1		4.14	4.20	1.014
	1	6.25	6.31	1.010
2		8.64	8.31	0.962
	2	11.35	11.51	1.014
3		13.72	13.48	0.983
	3	16.42	16.68	1.016
4		18.97	18.80	0.991
	4	21.22	20.79	0,980
			Average	0.996 ± 0.016
			0-0	1.25 ₅ Å.

TABLE VIII





Ozone

TABLE IX

л _о к	$\log K = \log p_{0_2}^{3/2} / p_{0_3}$	$(\underline{F}-\underline{E}^{o}_{\sigma})_{0}$	$(\underline{F}-\underline{E}^{o})_{0_{2}}$	s _{t+r} 56.41
298.16	28.486	48.545	42.058	S _v 0.38
500	18.482	52,966	45.662	Bits francisco a con a con particular a cana a con a
1000	11.122	59.646	50.675	
1500	8.664	64.041	53.779	s _{tot} 56.79
2000	7.434	67.352	56.070	\pm 0.1 cal/ $^{\circ}$ /mol
2500	6.694	70.024	57.901	
3000	6.207	72.255	59.431	

Pressure expressed in atmospheres.

 $(F-E_0^0)$ expressed in calories.

The curve marked M 127° was calculated for a mixture of 30 mole $\% 0_2 (0-0 = 1.21 \text{ Å})$ and 70 mole $\% 0_3 (0-0 = 1.27 \text{ Å})$ to show that even a relatively large impurity would not seriously falsify the results of this investigation. If the pictures had been taken of this mixture, the error would be an underestimation of the 0-0 distance by about 0.015 Å. and of the 0-0-0 angle by about 3°. As set forth above, however, there is ample reason for believing that the ozone was quite free of impurities.

Using the moments of inertia of the structure given above the entropy of ozone was calculated, and the equilibrium constant of the reaction $O_3 = 3/2 O_2$. The frequency assignments of Penney and Sutherland (29) were accepted in evaluating the vibrational entropy. The choice of any other recent frequency assignment would make a negligible change in the results. The value given by Stuart (30) of $E_0^0 = 34513$ cal/mole was used. The results are given in Table IX.

Since this work was completed, a paper by R. S. Mulliken (32) has appeared giving support to the structure of Hettner, Pohlman, and Schumacher (33), (based on spectroscopic evidence) which consists of an acute isoceles triangle with apical angle 39° and 0-0 bond distances 1.12 and 1.68 Å. The oxygen atoms at the base of the triangle are pictured not unlike 0^+_2 or 0^{++}_2 bonded loosely to an 0 or 0 at the apex. Such a molecule would have a very large dipole moment (perhaps in excess of 7 Debye units), and would certainly exhibit the abnormal physical properties of a strongly polar substance. Ozone shows no abnormalities, possesses a normal boiling point and vapor density. Although the radial distribution curves already exclude this structure, theoretical scattering curves were calculated for the 39° model. Agreement could not be obtained for this or any mixture of the model with oxygen.

Discussion. The resonating structures of ozone which are probably most important are the structures I-IV. Other singly bonded structures



are neglected because they place a doubly positive formal charge on the central oxygen, and the structure involving two double bonds would put ten electrons on the central oxygen atom. The angle found for ozone, 127° , is slightly larger than would be expected from the structures I-IV. The van der Waals diameter of oxygen in non-hydrogen-bonded molecules is about 3.0 $\stackrel{\circ}{}$.; in ozone the non-bonded oxygen distance is only 2.24 $\stackrel{\circ}{}$. and hence the electron clouds, particularly in the double-bonded structures, would repel each other strongly, tending to increase the angle. The combination of structures III and IV contribute nothing to the dipole moment, which must be largely due to I and II. If one assumes the oxygen single bond radius 0.73 $\stackrel{\circ}{}$. found in hydrogen peroxide (34) and the double bond radius 0.55 $\stackrel{\circ}{}$. (35) then, using the value 1.26 $\stackrel{\circ}{}$. found in this research for the 0-0 distance in ozone, the amount of double bond character is found to be approximately 30% (36). The calculated dipole moment is then $1.62 \ge 10^{-18}$ e.s.u., compared with the observed value $0.49 \ge 10^{-18}$ e.s.u. measured in a solution of liquid oxygen and ozone(37). A possible explanation of the small observed moment may be that the unshared electron pair on the central oxygen atom occupies an orbital such that it more than tancels the similar effect of the unshared pairs of the peripheral oxygen atoms and hence partially balances the moment of the positive formal charge of the central oxygen atom.

<u>Summary</u>. The electron diffraction investigation of ozone shows that the molecule is of the form of an isoceles triangle with 0-0 bond distance 1.26 \pm 0.02 Å. and 0-0-0 angle 127° \pm 3°.

(b) <u>Dimethyl peroxide</u>. The molecular structure of the peroxides has been a question of considerable interest. The configurations which have been proposed for peroxides are I and II.



For the organic peroxides structure I is now generally accepted (38). For hydrogen peroxide recent evidence from infrared spectrum (39), Raman spectrum (40), and dipole moment data (41) has eliminated structure II.

-58-

Penney and Sutherland (42) predicted on theoretical grounds that the structure I should have the configuration in which the angle 9 between the planes of the R-O-O- groups is about 100° rather than being either cis or trans with respect to the substituent groups. This structure accounts for the dipole moment and spectrum of hydrogen peroxide. The spectroscopic investigations of Zumwalt and Giguere (39) were interpreted on the basis of structure I, in which the molecule is neither cis nor trans ($\theta = 0^{\circ}$ or 180°) nor in the range for which 85° 4 9 4 95°. The electron diffraction investigation of hydrogen peroxide (34) gave the 0-0 distance 1.47 \pm 0.02 Å. A determination of the crystal structure of the addition compound of hydrogen peroxide and urea (43) gives the 0-0 distance 1.46 \pm 0.03 Å., and shows that the configuration of the Hoo, molecule is essentially that proposed by Penney and Sutherland, with $\theta = 106^{\circ}$. (The hydrogen atoms were assumed to lie along the direction of inferred hydrogen bonds.)

The present investigation was undertaken with the object of obtaining an average of the C-O and O-O bond distances for comparison with that found in the ozonides. It was at first not expected that the angle Θ could be determined, since in an electron diffraction investigation of the more favorable case of sulfur monochloride, S_2Cl_2 , which presumably has the same structure as dimethyl peroxide, no decision was reached regarding the orientation of the chlorine atoms relative to each other (44). In view of the results on dimethyl peroxide it is likely that the present improved technique would make a reinvestigation of S_2Cl_2 profitable. It is also suggested that an investigation of the molecule F_2O_2 (45) would give more information in this direction that any other simple peroxide.

Experimental. The dimethyl peroxide was prepared by the method of Rieche (46) by the reaction of hydrogen peroxide with dimethyl sulfate in the presence of potassium hydroxide. About 3 ml. of the product was redistilled, and 1 ml. boiling at 14° at 745 mm. was collected in a trap cooled in a dry ice and acetone mixture. A bulb of about 250 ml. capacity, which could be removed and attached to the electron diffraction apparatus with a standard glass taper, was then filled to a pressure of 450 mm. with gaseous dimethyl peroxide. The electron diffraction photographs were made at room temperature. The camera distance was 10.93 cm., and the wavelength of the electrons was 0.0610 Å.

Interpretation. The radial distribution function, marked RD in Fig. 8, showed strong peaks at 1.11 Å. (C-H), 1.44 $_{5}^{\circ}$ (average of C-O and O-O), and 2.30 Å. (C···O), indicating an O-O-C angle of about 105°. The radial distribution function can be fitted by either structure I or II; for the latter the resulting structure would be decidedly pyramidal. In view of the evidence referred to above only models based on structure I were considered, although it is possible that as good agreement

-60-

could not be obtained for structure II because of the absence of the long C···C and X···H terms which appear in I. No information about the relative orientation of the methyl groups is given by the radial distribution curve. This can hardly be expected, since the terms in the theoretical intensity function which are dependent on the relative orientation of the methyl groups about the O-O axis amount to less than 8% of the total molecular scattering, and undoubtedly have a considerable temperature factor. Even a small libration would effectively broaden and suppress such an expected peak.

In calculating the simplified theoretical intensity curves the C-H distance was assumed to be 1.09 Å., and the H-C-H angle was taken to be $109\frac{1}{2}^{\circ}$. The temperature factor constant a was taken to be 0.00015 for bonded C-H terms, 0.00030 for short non-bonded 0^{•••}H terms, and approximately 0.00090 for long non-bonded C^{•••}H and O^{•••}H terms, and 0.0 for all others.

The assumption was made that the long interactions could be lumped together at average C···H and O···H distances (in the neighborhood of 2.60 and 3.80 $\stackrel{0}{\text{A}}$), and be given a strong temperature factor. This assumption is not entirely satisfactory, and a more exact treatment would require some additional assumptions about the relative orientations of the methyl groups, or the use of some approximation

-61-

to freely rotating methyl groups. By using one of these other distributions of C ··· H and O ··· H distances the apparent fit to the radial distribution function would not be as good: in any event the long C ... C term is more important than the long X ... H terms in causing improvement of the theoretical curves in the neighborhood of q = 30 to 40 for the models described below. If the normal C-O bond length 1.43 A. is assumed, the 0-0 bond length calculated from the radial distribution peak at 1.445 Å. is 1.47 Å., in good agreement with the 0-0 distance found in hydrogen peroxide (34). Curves were calculated in which the C-O/O-O ratio was varied from 1.40/1.50 to 1.48/1.40, and the angle C-O-O varied from 100 to 110° , with various values of Θ , the angle between the planes of $C_1 - O_2 - O_2$ and O-O-C2. Some of these curves are shown in Fig. 8. The procedure followed consisted in calculating theoretical curves in which the terms dependent on rotation were omitted. These curves represent essentially models with free rotation of the methyl groups about the 0-0 axis. Since the rotation dependent terms are only of the order of 8% of the total molecular scattering, it was obvious which curves could be brought into better agreement with the visual curves by adding the rotation dependent terms. The parameters of the various curves are given in the legend of Fig. 8. From these curves it can be seen that a variation of 5° in either direction from 105° of the

-62-

angle 0-0-C is sufficient to produce disagreement with the observed pattern. Static "cis" models were all unsatisfactory, although static models in which the angle 9 was between 125° and about 150° (models K, L, M, and O) were acceptable for values of the C-O/O-O ratio of from 0.95 to 1.06. Corresponding models for methyl groups freely rotating about the O-O axis (curves C, E, and G) are not as satisfactory. This is consistent with a moderately large barrier restricting rotation and a correspondingly fairly small amplitude of libration of the methyl groups around a position about 45° from "trans".

Quantitative comparison of observed and calculated q values for Model L is shown in Table X. The average bond distance is $1.44_5 \pm 0.02$ Å., corresponding in model L to the C-O distance 1.43 Å. and O-O distance 1.47 Å. It is not possible to set interestingly small limits of variation on the separate bond lengths. The C-O-O angle on the other hand can be given as $105^{\circ} \pm 3^{\circ}$.

TABLE X

DIMETHYL PEROXIDE

.

Max	Min	q _o		q _c (L)	q _c /q _o
-	l	7.67		8.90	(1.160)
-	2	14.99		13.65	(1.002)
2	_	19.09		18.90	0.990
	3	24.26		24.20	0.998
3	۸.	30.15		30.50	1.011
١.	4	32.88		36.00	(1.095)
4	5	20.32		38.00	(1.046)
5	2	45.41		44.85	0.972
2	6	50.84		51.10	1.005
6		56.07		57.10	1.018
	7	58.56		58.90	1.006
7	đ	61.38		61.00	0.994
g	8	72 70		66.40 72 55	1.000
0	9	78.02		77.75	0.998
9	,	86.28		87.90	(1.019)
-	10	94.62		94.00	0.994
10		99.76		98.90	0.992
			Average		0.999
			Average	Deviation	0.009







Dimethyl Peroxide

Model	C0	0-0	∑ 0-0-C	∑ c ¹ oc ⁵ = 0
A	1.40	1.50	1 05 ⁰	Free rotation
в	1.43	1.47	100	11
C ·	1.43	1.47	105	"
D	1.43	1.47	110	11
E	1.46	1.43	105 30'	11
F	1.48	1.40	101	17
G	1.48	1.40	106	11
H	1.48	1.40	111	11
I	1.43	1.47	105	0° (cis)
J	11	11	ที่	115
K	Ħ	н	11	125
L	ŧ	н	11	135
М	18	15	11	145
N	11	11	11	180 (trans)
0	1.46	1.43	105 30 '	135

(c) The Molecular Structures of Ethylene Ozonide and 2-Butene Ozonide The question of the configuration of the ozonides has long been a subject of considerable investigation and discussion (47). The simple ozonides boil at low enough temperatures that an electron diffraction investigation seemed promising as a means of obtaining further information on the structure of the ozonides, and ethylene and 2-butene ozonides were accordingly investigated. The structures which have been proposed to account for the chemical properties of the ozonides are I-IV.



The chemical evidence may be summarized briefly as follows:**

(1) The normal ozonide contains threeadded oxygen atoms per double bond.

(2) After ozonization the original compound cannot be regenerated.

(3) On gentlest possible reduction, whether with hydroquinone,

hydrazobenzene, aluminum amalgam, zinc dust and silver nitrate, or catalytic hydrogenation at 0° C., no glycol of the type -C(OH)C(OH)-

has been obtained.



- * This structure would now be written as
- ** The original references will be found in the review articles of reference (47).

-67-

(4) The decomposition products of the czonides of ethylene, butylene, and oleic acid have been shown to contain the group -CH(OH)-O-O-CH(OH)-.

(5) A material claimed to be identical with butylene ozonide has been synthesized by the dehydration of dihydroxy ethyl peroxide, $CH_{3}CH(OH)-O-O-CH(OH)CH_{3}$.

(6) The ether linkage in amylene ozonide has been identified by use of the sodium malonate reaction of Lehmann (52). These facts can best be explained by the structure IV, in which the double bond is completely split and the carbon atoms are separated by ether and peroxide linkages. Evidence in favor of this structure is also given by the heat of ozonization data of Briner and his collaborators (53). Their experimental data are given in Table XI. The heat of ozonization depends on the types of bonds formed in the reaction, and consequently should be considerably different for the two structures III and IV, which would result from the following reactions:



The heats of reaction were calculated from the difference of bond energies on the two sides of the equations using the values given by

-68-

TABLE XI

HEATS OF OZONIZATION

 $(R + O_3 \rightarrow R^{\circ}O_3 + \Delta H.$ Determined from heats of combustion of ozonides. (53))

R	- A H
Allyl Benzene	119, 116, 124
Estragol	114, 119, 120
Eugenol	113
Isoeugenol	113, 116, 117
Safrol	113, 115
Isosafrol	111, 110
Anethol	125, 132, 128
Ethyl maleate	86
Ethyl fumarate	115, 114
Methyl citraconate	112, 110, 111
Methyl mesaconate	127, 134, 133
Avera ge	117 ± 6
Pauling (54) for the bond energies of C=C (100 kgcal mole⁻¹), C-C (58.6), C-O (70.0), and O-O (34.9), and 143.3 for the heat of formation of ozone from oxygen atoms (55). Account was also taken of an additional stability of the 0-C-0 grouping which is not represented by the bond energies. This correction was determined from the heats of combustion of the following substances to be, per 0-C-0 group: dimethyl acetal, 14.5; diethyl acetal, 21.3; methylal, 22.6; diethyl methylal, 21.4; glycol methylal, 14.3; trioxane, 23.7; and paraldehyde, 18.1; average, 19.4 kgcal mole⁻¹. Five kgcal has been added to the calculated heat of ozonization in each of the reactions III and IV above to account for an estimated difference in heat of vaporization of the ozonide and the olefin. It is likely that the 0-0 bond energy, which was obtained (54) from the heat of formation of hydrogen peroxide, may also be subject to a correction for use with alkyl peroxides and ozonides. No data on such peroxides are available at present. For aryl substituted hydrazines (56) the N-N bond energy does not change much from the N-N bond energy in hydrazine, although the situation is probably different in the alkyl series, for which the higher members are more stable toward dissociation than hydrazine (57). It is unlikely, however, that the effect would be large enough to bring III into agreement, or to put II in serious disagreement, with the observed heat of ozonization. A correction of about 8 kgcal mole for the $^{\circ}$ C - C $^{\circ}$ grouping in structure III is indicated by the

-70-

heat of combustion of dioxane. The heat of combustion of glycol methylal on the other hand, which contains in addition an O-C-O group, does not indicate such a large correction, so that the value of 30 kcal calculated for III may have an additional uncertainty of about 5 kcal. We believe these estimates are reliable enough to rule out structure III, if the calorimetric data are accepted. For structures I and II no reliable estimates of heats of ozonization can be made, since no other stable compounds of this type are known for comparison. Some correction to the O-O and C-O bond energies for the $\sum_{i=1}^{i} - \sum_{i=1}^{i}$ group would be necessary, but aside from this correction I and II would stand in the same stability relation as III and IV respectively. Since structures I and II are eliminated by the electron diffraction data they are not considered further.

Experimental. Ethylene ozonide was prepared by the method of Harries and Koetschau (58) by the ozonization of ethylene in liquid methyl chloride at -78° C. in an all-glass apparatus as shown in Fig. 9. About 5 ml. ethylene (b.p. -104° C.) and 150 ml. methyl chloride (b.p. -24° C.) were condensed in the trap A by means of liquid air, which was then replaced by a dry-ice and acetone cooling bath. Tank oxygen was passed through the drying tubes and ozonized in a silent electrical discharge at 0° C. The dilute ozone thus produced passed through a coil cooled with dry-ice acetone mixture, and bubbled through the solution of ethylene. At the appearance of a faint blue color



Figure 9

czonization was stopped. The methyl chloride was allowed to evaporate off at room temperature, the last traces being pumped off while the trap A was held at about -10° C. Of the remaining clear colorless liquid, in amount about 3 ml., about 2 ml. was distilled over into Trap B, leaving a very viscous polymerized material which exploded when heated to about 45° C. About one-fourth of the material in the trap B waspumped off, after which one ml. was condensed in the bulb C (vapor pressure at 20° C. about 20 mm.). This bulb œuld then be removed and attached to the electron diffraction apparatus. The dry purified ozonide (liquid) was quite sensitive to rapid changes of pressure; it also exploded violently upon heating to 40° at atmospheric pressure.

2-Butene ozonide (59) was prepared in the same manner as described above, from trans-2-butene (60). Three ml. of the product was distilled from A to B; about 0.5 ml. of this was pumped off, and 1 ml. distilled at 25° C. and 25 mm. pressure was condensed into C, which was then removed and attached to the electron diffraction apparatus.

Attempts to prepare the ozonide of 1,2-dichloroethylene by this method were also made. Upon evaporating off the methyl chloride solvent after ozonization, a clear, slightly yellowish liquid remained. In a short time this began to evolve a colorless gas and exploded spontaneously. After three attempts, each resulting in the destruction of the apparatus, the preparation was abandoned.

-73-

The electron diffraction photographs of both ethylene and 2-butene ozonides were made at about 25° C. with the low temperature nozzle. The wave length of the electrons was about 0.061 Å. and the camera distance was about 10.9 cm. Corrections were made for film expansion.

The visual appearance of the photographs is Ethylene ozonide. represented by the curve V of Fig. 10. It resembles the general appearance of photographs of other molecules containing a 5-membered ring. (See ethylene methylene dioxide and pyrazolidine, above, and pyrrole, thiophane, and furan (61).) The radial distribution function marked RD shows peaks at 1.44 A. and 2.25 A., the former an average of C-O and O-O bond distances. These distances indicate an average angle of about 103° (2.25 = 2 x 1.44 sin 103° /2). The fourmembered ring structures I and II, are eliminated by the radial distribution function, since for them one would expect three strong peaks. Unlike methylene cyclobutane and methyl cyclobutene (see above, especially the radial distribution curves of Figures 1 and 2) these structures would not be planar, but the distances involved are such that the radial distribution function would be expected to show three main peaks nevertheless. The structures III and IV, the only other structures that have received serious support, are in general agreement with the radial distribution function although the average

-74-



Ethylene Ozonide

Figure 10

Legend for Figure 10

Model	Type	8	၉	Y	θ	ф	C-0	0-0	C-C
A	IV	106°	111.5°	105 [°]	(Planar)		1.43	1.48	1.54
.B	IV	110	100.5	118.5	(Planar)		"	11	11
С	IV	105	105	102	41°	0	11	II	11
D	IV	104	104	99	48	0	11	11	IL
Ε	IV	104	100.5	108	0	30 [°]	11	11	11
F	III	97•5	106	102	0	34	1.40	1.45	1.51
G	II	Square	me thylcyc	lobutane-	-like struc	ture,	1.43	1.48	
		<u> ∠</u> c-o-¢	> = 1 19°						

 θ is the angle between the plane of $\propto \sigma \beta \beta$ and the plane of $\beta \gamma \beta$ ϕ is the angle between the plane of $\alpha \gamma \sigma$ and the plane of $\beta \gamma \beta$ (o below and x above the plane of $\beta \gamma \beta$). bond angle 103°, being some what less than 108° as required for an approximately symmetrical planar pentagonal model, indicates a nonplanar ring. Although we simply assume both for ethylene and butylene ozonide that the molecules do not have an open chain structure, it may be remarked that it would be difficult to understand why in an open chain structure the average bond angle should be so small as 103° (or 105; see below). For the five-membered ring structures, on the other hand, the unusually small bond angle may come about merely as the geometric concommitant of the non-planarity of the ring, which may be caused by an intermolecular potential of rotation about the single bonds. According to Penney and Sutherland (42) this potential for the peroxide group would make the planar cis configuration unstable relative to a configuration formed by an internal rotation of 100° by about 10-20 kcal/mole. Thus it is not unreasonable that the forces associated with this potential are large enough to cause some deviation from planarity. If the normal bond distances C-O = 1.43 A., C-C = 1.54 A., and O-O = 1.47 A. are assumed, the average of bond distances for structure III is 1.465, and for IV it is 1.440. A reduction of all the bond distances by 0.02 Å. or of the C-O or C-C bond length by 0.03-0.04 Å. would be required to bring model III into agreement with the observed radial distribution peak at 1.44 Å. It is quite possible that the C-O or C-C distance is shorter than normal (as for example in trióxane or dioxane, above), or that the average bond distance from the radial distribution function is in

-77-

error by as much as 0.02 Å., so that this argument cannot be used to decide between structures III and IV, although it favors the latter.

Theoretical intensity curves were calculated for the structures III and IV assuming the normal bond distances C-0 = 1.43 Å., O-0 = 1.43 Å., and the configuration

and the parameter values given in the legend to Figure 10. The E-C-H angle was taken to be 116° , and the C-H bond length 1.09 Å. Good qualitative agreement with the visual appearance of the photographs could not be obtained for planar models (A and B of Fig. 10 and intermediate curves not shown). Non-planar models were made in two different manners: either by keeping four atoms in one plane and moving the other out of that plane (C and D, Fig. 10), or by keeping three atoms in one plane and placing one atom above, and one atom below that plane (E and F, Fig. 10). The latter process is equivalent to twisting the bond joining two atoms about the line bisecting the bond angle of the other three atoms. This configuration would probably be assumed if the bonds of the -O-O- grouping prefer to be arranged in the manner calculated by Penney and Sutherland (42) and indicated in the crystal of hydrogen peroxide-urea (43), namely, with an angle of about 105° between the planes of the OH groups. Best agreement

TABLE XII

ETHYLENE OZONIDE

Max	Min	d ^o d	l _c (E)	q_c/q_o (E)	q _c (F)	q _c /q _o (F)
1	l	6.53 11.37 1	7.00	(1.072)	8.20 12.45	(1.256)
2	2	15.38 1 20.00 1	4.50.	(0.943)	15.50	(1.008)
3	3	24.70 2 30.13 2	24.60	0.996	24.90 29.90	1.008
4	4	33.78 3 38.09 3	4.60 6.75	(1.024) (0.965)	35.80	(1.059) (0.998)
5	5	42.30 3 46.41 4	9.95 5.50	(0.944) 0.980	40.35 45.90	(0.954)
6	6	51.51 5 56.94 5	51.00 56.80	0.990 0.998	51.60 57.15	1.002
7	7	60.05 5 63.43 6	9.90 2.00	(0.998) (0.977)	60.60 63.15	(1.009) (0.996)
g	8	66.92 6 71.70 7	7.00 2.60	1.001	68.00 73.50	1.016
	9	78.49 7	8.05	0.994	79.00	1.006
		Average Average De	viation	0.993 0.008		1.003 0.010
		C-0 0-0 C-C		1.420 1.470	3	1.40 1.455 1.515

for either structure type III or IV was obtained for this configuration (E and F, Fig. 10) but it is not certain that nearly as good agreement could not be bbtained with models of the type of C and D which themselves are not wholly unsatisfactory. The qualitative appearance of curves E and F is nearly indistinguishable. By superposition of several films it was possible to see the cuter features in the region q = 50 - 100, which consisted of a broad double maximum followed by a strong single peak as in E and F. No measurements were made on these features, however. Quantitative comparison of observed and calculated q values is given in Table XII for models E and F. It is seen that no decision can be made between structures III and IV on the basis of either the qualitative comparisons or the internal consistency of the quantitative comparison; but the definite conclusion that the ozonide structure is a non-planar five-membered ring can be drawn.

<u>2-Butene ozonide</u>. The positions of the carbon atoms not having been uniquely determined in the investigation of ethylene ozonide, it was hoped that a suitable 1,2-derivative of ethylene would give further information. Such a compound is 1,2-dichloroethylene ozonide, which should show a radial distribution peak corresponding to a long chlorinechlorine interaction, whose distance would be quite different for the two structures III and IV above. As mentioned, however, the product of ozonization of 1,2-dichloroethylene was too unstable to isolate

-80-

satisfactorily. As the most simple alternate, trans-2-butene ozonide was investigated. It was not expected that 2-butene ozonide would give much more definite information than ethylene ozonide, since the substitution of two methyl groups does not markedly alter the structure, or contribute enough additional scattering to resolve the long methyl-methyl interaction (as would doubtless be possible with chlorine atoms).

The visual appearance of the photographs, shown by curve V, Fig. 11, resembled closely that for ethylene ozonide. The seventh minimum appeared broad and sloping gradually from the sixth and seventh maxima as shown, rather than having subsidiary features on the sides of the maxima (as in curve G). The eighth and ninth maxima were definitely doubled, although it was difficult to decide which was the stronger peak.

The radial distribution curve, marked RD, has two well-defined peaks at 1.445 $\stackrel{\circ}{\text{A}}$ and 2.28 $\stackrel{\circ}{\text{A}}$, indicating an average bond angle (C-C-O, C-O-C, O-C-O, and O-O-C) of about 105°. These distances are compatible with a puckered five-membered ring structure. If the normal bond lengths C-O = 1.43 $\stackrel{\circ}{\text{A}}$, O-O = 1.47 $\stackrel{\circ}{\text{A}}$, and C-C = 1.54 $\stackrel{\circ}{\text{A}}$. are assumed, the weighted average bond distance is 1.48 $\stackrel{\circ}{\text{A}}$ for structure III, and 1.46 $\stackrel{\circ}{\text{A}}$ for structure IV. It is apparent that there is some bond shortening on the basis of either model, but it is not conclusive. For example, a deviation from the usual C-O distance as great as that found in trioxane (C-O = 1.40 $\stackrel{\circ}{\text{A}}$; Section C-d) would be sufficient

-81-



Figure 11 2-Butene Ozonide

.

Legend for Figure 11

V Visual Curve RD Radial Distribution Curve (upper distances Model I, lower distances Model Q) ð 8 1 ď ß C-0 0-0 C-C 0 0 106° 0 111° 1.54 105 1.47 1.43 110 0 A 11 В = 11 108 107 110 110 0 11 11 11 С 109 103 115 110 0 H D 11 = 101 101 110 110 30 1.40 1.46 1.54 102 20 Ε 108 105 1091 F 11 11 = 30 99 105날 105 109불 11 " 11 G 1003 1013 110 1091 30 1.46 1.43 1.50 100 106 30 Η 105 109불 1091 25 11 I* 1.40 1.54 100 1051 107불 25 25 25 0 11 11 11 J 101 1053 1091 107 1.54 K 1.41 11 100 104% 108날 109불 L 1.43 1.47 1.54 106 111 30' 105 112 11 116 0 М 11 11 1091 102 1093 1.47 1.43 1.54 1051 25 N 103 110 110 99¹/₂ 103 35 11 11 11 0 983 110 110 1.44 97 P 1.40 1.50 105 106; 111호 35 1.40 1.45 1.48 98 1041 105 30 Q* 108; 114

· Models A to K inclusive, Type IV, Staudinger model N arriesmodel

The angles $\phi, \beta, 1, \delta$ are defined by Fig.

* Models I and Q were the most satisfactory models.

Curve

Models	L	to	Q	inclusive,	Type	III,	Ha

to bring the average for structure IV to 1.445 Å. For structure III somewhat greater reductions are necessary, such as of all the bond distances by about 0.03 to 0.04 Å., to produce agreement with the radial distribution peak. Since the main features of the distance spectrum of either structure can be made very close to that of the other, either can be fitted to the radial distribution curve with appropriate values of the bond distances and angles. However, it has been possible to get a better fit to the region of 3 Å. to 4 Å. with structure IV. Moreover, if III is correct, then the distances and angles required to fit the radial distribution peaks are unusually small compared to those normally found. (The difference in angles arises in fitting the 2.28 Å. peak, because the average bond distance is not related to the average X···Y distance by the average bond angle, and because two C-C-O angles in structure IV are replaced by C-C-C- angles in structure III.)



In calculating the simplified theoretical intensity arves it was assumed that the ozonide was an equimolar mixture of the cisand trans-compounds with respect to the orientation of the methyl groups. This assumption was made in the lack of better information about the actual course of ozonization of the starting material, which was about 85% trans-2-butene. This affects the long interactions of the ring atoms with the methyl groups, which in any case are not very important. The C-H distance was taken to be 1.09 Å. with temperature factor constant $a_{i,i} = 0.00015$. In calculating curves for non-planar models the non-planarity was attained for both types III and IV by twisting the O-O groups relative to the adjacent bonds so as to place one O above (o) and one O below (x) the plane of the other three atoms, in the manner expected on the basis of the Penney-Sutherland structure of the peroxide group. Non-planarity could be achieved in other ways, which would however give essentially the same result. No systematic variation of the parameters was attempted, both because of the large number of parameters, and because of the large variations which no doubt are allowable for some of them. The parameters which were varied were the bond lengths, one angle of the ring (the others are determined if the bond lengths are given), and 0 the angle of rotation of the 0--- 0 group about the axis indicated in III and IV above. Other parameters such as the angles C-C-CH_z or O-C-CH_z were then adjusted to give the best fit with the radial distribution peak at 2.28 Å. The correlation procedure here was not so much used to set limits on the variation of parameters (although it gives some idea of the variation allowed) as rather to show that good agreement actually can be obtained. The attempt was made throughout to keep angles and bond distances as consistent with the accepted results of structure

-85-

investigations as possible. Agreement can probably be obtained for other values of the parameters than those given, since a rather large number of parameters is available.

Good agreement with the visual curve could not be obtained for planar models, as was found with ethylene ozonide. For models of Type IV agreement could be obtained by making the molecule non-planar. For models of Type III unusually short bond lengths and small bond angles are required to produce acceptable curves. Even then, agreement for the outer half of the pattern was not entirely satisfactory; neither the characteristic shape of the broad seventh minimum nor the doubled outermost maximum is well represented by curve Q the best of this type. However, it is not obvious that better agreement could not be obtained.

Some of the theoretical intensity curves which were calculated in the search for satisfactory models are shown in Fig. 11; the values of the parameters used in calculating them are given in the legend to Fig. 11. Comparison of observed and calculated q values for the most satisfactory curves of each type (I and Q) is given in Table XIII. The distances in these models are given under the radial distribution curves, I above and Q below.

-86-

TABLE XIII

2-BUTENE OZONIDE

Max	Min	q _c (I)	^q obs	q _c /q _c (I)	۹ ₂ (۹)	۹ ₀ /۹ ₀ (۹)
2	2	7.95	7.68	(1.035)	7.25	(0.944)
L.,	3	14.60	15.06	(0.969)	14.10	(0.936)
3	31	19.00	18.98	1.001	18.75	0.988
4	. 4	24.20	23.95	1.010	24.10	1.006
	5	33.60	32.53	(1.032)	33.40	(1.027)
5	6	35•75	36.43	(0.981)	36.00	(0.988)
6	0	45.70	45.63	1.002	45.20	0.991
-7	7	51.90	50.86	1.020	50.75	0.998
1	g	50.50 66.30	57•15 65•77	1.008	57•40 66•00	0.994 1.003
ଞ		75.00	74.90	1.001	73.40	0.980
a	9	80.20 85.00	79•32 85.60	1.011	79.50	1.002
)	10	88.60	90.03	(0.984)	89.60	(0.990)
10		92.80	94.26	(0.985)	92.10	(0.977)
11	11	97.50 102.3	99•13 103•27	0.984 0.991	95.50 101.50	0.963 0.983
		Average		1.004		0.993
		Average I)eviation	0.008		0.010

×.

•

Evidence on the structure of the ozonides may be Summary. summarized as follows. Very extensive chemical evidence has restricted the possibilities to either four or five-membered ring structures, with the ether-peroxide bridge structure IV of Staudinger giving the best explanation of the chemistry of the ozonides. The electron diffraction results are compatible with a five-membered ring, but eliminate the four-membered ring structures I and II. It is also clear that the five-membered ring in the ozonides of ethylene and 2-butene is non-planar. The arrangement of the oxygen atoms relative to the carbon atoms has not been uniquely determined. Although agreement with the observed pattern can be obtained for both structures III and IV, it is actually somewhat better for IV than for III. In addition, the distances required to produce agreement for III are less consistent with distances normally found than are those given by IV, which indeed are practically normal. The heat of combustion data presented above also provide support for structure IV. There can thus be little doubt that structure IV accounts best for all known evidence on the structure of ozonides.

-88-

The Molecular Structure of some Halogenated Ethanes.

The fluorochloroethanes are of interest with regard to the question of the restriction of rotation about the C-C bond (62,63). Since in a preliminary investigation it was found not possible to account for the diffraction pattern of $CF_2OI \cdot COl_2F$ by assuming the distances and angles found for the fluorochloromethanes by Brockway (64), an investigation of the simpler methyl compounds was undertaken.

Experimental. The compounds were obtained from Dr. A. F. Benining of the E. I. duPont de Nemours Co., Electrochemicals Division. They had the following physical constants: CH_3CF_3 , m.p. -107° , b.p. -47° ; CH_3CF_2CI , b.p. -9° ; CH_3CFCI_2 , b.p. 31.8° C. The wavelength of the electrons, determined from transmission photographs of gold foil, was 0.0615 Å., the camera distance was 10.90 cm. The pressure of the gases in the storage bulb on the electron diffraction apparatus was about one atmosphere.

(a) <u>Methyl</u> <u>Fluoroform</u> (CH_3CF_3)

The photographs showed the rings and had the visual appearance shown by the curve marked V in Fig. 12. The radial distribution curve, marked RD, had maxima at 1.03 Å. (C-H), 1.37 Å. (C-F), 2.19 Å. (F···F), and 2.40 Å. (C···F). These values give calculated angles F-C-F 106° , and C-C-F 112° . Theoretical intensity curves were calculated using the usual formula and C-H temperature factor coefficients. In calculating the theoretical curves it was found that the F···H terms

-89-



Figure 12 Methyl Fluoroform

-90-

Legend for Figure 12

Methyl Fluoroform (CH3CF3)

v v

RD

.

Visual Curve Radial Distribution Curve

	C-F	C-C	∠ F-C-F	∠ c-c-f
A	1.37	1.56	104°441	113°56'
В	16	1.51	14	11
C	11	1.48	14	11
D	11	1.58	106	112 50
E	11	1.54	11	11
F	11	1.52	11	13
G	11	1.59	107	111 55
H	18	1.56	. 16	11
I	ti	1.54	11	11
J	11	1.50	11	ff
K	18	1.48	11	11
L	H	1.58	108 30	110 30
М	14	1.55	11	11
N	88	1.52	17	11
0	H .	1.48	108	111
P	18	1.59	109 28	109 28
Q	H.	1.57	"	11
R	11	1.54	11	11
S	11	1.48	109	110

depending on rotation had only a small effect even at small scattering angles; the staggered configuration of the $-CH_3$ and $-CF_3$ groups relative to each other was therefore assumed and the longest F ... H interactions neglected. Curves were calculated for C-F = 1.37 Å. and C-C varying from 1.48 to 1.59 Å. for various values of the angle F-C-F. (The angle C-C-F is determined by the angle F-C-F if trigonal symmetry is assumed.) A sufficient number of a rves was calculated to assure a complete two-parameter variation treatment. Some of these curves and the values of the parameters used in calculating them are given in Fig. 12. The sixth and seventh maxima appeared to be about equal and doubled as shown; the seventh maximum may in fact be slightly higher than the sixth. The range of variation of the angles is seen to be about four degrees. For the angle $F-C-F = 107^{\circ}$ considerable range in the variation of the ratio C-F/C-C is allowed. This means that the scattering of the ${\rm CF}_{\rm Z}$ group dominates the scattering by the molecule, so that the uncertainty in the C-C distance is much greater than that in the C-F distance. Best agreement was found for curve I. Quantitative comparison of observed and calculated q values for curve I is given in Table XIV. The final results are $C-F = 1.36 \pm 0.02 \text{ Å}$. $C-C = 1.53 \pm 0.04 \text{ Å}$, $\angle F-C-F = 107^{\circ} \pm 3^{\circ}$, and $\angle C-C-F = 112^{\circ} \pm 3^{\circ}$.

-92-

TABLE XIV

METHYL FLUOROFORM CH3CF3

Max	Min	₫ ₀	$q_{c}(H)$	$q_{c}^{\prime}/q_{o}^{\prime}(H)$	$q_c(I)$	q _c /q _o (I)	q _c (J)	q _c /q ₀ (J)
1	l	7•37 10•99	7.30 11.10	(0.991) (1.010)	7.40	(1.004)	7.00 10.70	(0.950)
_	2	14.88	14.60	(0.981)	14.70	(0.987)	14.30	(0.961)
2	3	19.34 24.33	19.50 24.55	1.008	19.45 24.50	1.005	19.15 24.75	0.990 1.017
3),	29.37	29.60	1.008	29.60	1.008	30.20	1.028
4	4	37.61	36 . 95	(0.982)	35.80 36.50	(0.970)	54•75 37•60	(1.045) (1.000)
F	5	42.21	41.75	0.989	41.50	0.983	42.30	1.023
5	6	53.29	53.60	1.006	53.50	1.004	53.50	1.004
6	7	59.04 62.93	58.60 62.45	0.993	58.75 62.50	0.995 0.993	58 .90 62.20	0.998 0.988
7	, ,	66.32	66.05	0.996	66.20	0.998	66.10	0.997
ଝ	8	76.88	76.00	0.990 0.989	76.00	0.990	71.15 76.10	0.992
0	9	81.94	80.50	0.982	80.65	0.985	80.50	0.983
. 9	10	- 10	87.90		88.25	0.972	88.10	0.900
10		94.36	92.80	0.984	93.10	0.987	92.60	0.981
	Aver Aver	age age Devia	ation	0.994 0.009		0.994 0.008		0.997 0.013

(b) <u>Methyl</u> <u>difluorochloromethane</u> (CH₃CF₂Cl)

The photographs showed ten rings, and qualitatively had a similar appearance to the methyl fluoroform photographs. The visual appearance of the photographs is shown by curve V of Fig. 13. The radial distribution curve RD had maxima at 1.11 Å. (C-H), 1.36 Å. (C-F), 1.78 Å. (C-Cl), 2.19 Å. (F···F), and 2.57 Å. (C···F, F···Cl, C···Cl). These distances given calculated values of \angle F-C-F = 107° and \angle F-C-Cl = 109° (approximately). The same assumptions were made regarding the hydrogen terms as in fluoroform above. In addition, the C-C distance was assumed to be 1.54 Å., since no peak corresponding to this distance appears in the radial distribution curve.

Theoretical intensity curves were calculated for C-F = 1.36 Å., C-C = 1.54 Å., and C-Cl = 1.76 Å. In the neighborhood of curves which agreed with the observed pattern, curves were also calculated for C-Cl = 1.73 or 1.78 Å., and C-C = 1.51 Å. Agreement could be obtained in two different ways; first by assuming an equal distortion of the halogen angles by the methyl group, which required that the X-C-X angle be less than 109°, or secondly by expanding the Cl-C-CH₃ angle and assuming the strain to be taken up in the F-C-F angle, which then became less than 109°. The latter of these two models seems more plausible, from consideration of the van der Waals radii of fluorine, chlorine, and the methyl group. Curve A, Fig. 13 was calculated using the distance and angles found by Brockway () for difluorochloromethane.

-94-





Legend for Figure 13

Methyl	difluoroch	loromethane (C	H ₃ CF ₂ C1)		
	C-C1	∠ C-C-F	∠ c-c-c1	/ F-C-Cl	∠ F-C-F
A	1.73	108 [°] 30'	108 ⁰ 301	110°30'	110°30'
В	1.76	109 [°] 28′	109°28'	109°281	109°28'
С	1.76	111	111	108	108
D	1.76	111 55	111 55	107	107
E	1.78	108 48	108 48	112	107
F	1.76	109	109	111	108
G	1.76	110 26	110 26	109 8	107 14
н	1.76	109 54	111	109 28	107

Theoretical intensity curves and the values of the parameters used in calculating them are given in Figure 13. In view of the fact that agreement could be obtained in two ranges of two of the angle parameters, rather wide limits of error must be set on their probable values. Calculated and observed values of q for the two models C and F which agreed best with the observed pattern are given in Table XV. The distances used in model F are drawn under the radial distribution curve in Fig. 13. Since agreement could also be obtained with C-C = 1.52 by only slight changes in the angle parameters, the final values of the parameters are C-F = 1.37 \pm 0.03, C-C = 1.54 (assumed), C-Cl = 1.77 ± 0.03, \angle C-C-F = \angle C-C-Cl = 111° ± 5°, \angle F-C-F = \angle F-C-Cl = 108° ± 5°. Since the angle F-C-F is given uniquely, by the radial distribution peaks, the error in the value of this angle is probably somewhat smaller than that given for the others.

TABLE XV

METHYL	DIFLUOROCHLOROMETHANE	CH_CF_C1
		3 2

Max	Min	q _o q	(C) q	q _c /q _o (C)	а _с (F)	$q_{c}^{}/q_{o}^{}(F)$
_	1	6.51	5.70	(1.029)	6.50	(0.998)
1		9.89 10	0.00	(1.011)	10.20	(1.031)
	2	13.11 1	3.50	(1.029)	13.60	(1.038)
2		17.66 1	7.65	0.999	17.90	1.013
	3	21.68 2	1.75	1.003	22.20	1.024
3		25.19 2	5.70	1.020	26.00	1.032
	4	29.01 2	9•45	1.015	29.85	1.028
4		33.42 3	3.50	1.002	33.80	1.011
	5	36.46 3	7.80	(1.037)	37.60	(1.031)
5		39.70 4	0.50	(1.020)	40.75	(1.026)
	6	43.70 4	3.90	1.005	43.90	1.005
6		48.38 4	8.60	1.005	48.50	1.003
	7	52 .61 5	3.60	1.019	53.50	1.017
7		57.75 5	8.40	1.011	58.40	1.011
	g	62.14 6	2.30	1.003	62.20	1.001
8		66.30 6	5.50	0.988	65.45	0.987
	9	70.06 6	9.70	0.995	69.95	0.998
9		73.89 7	4.00	1.001	74.00	1.001
	10	76.63 7	7.10	1.006	77.50	1.011
10		81.32 8	1.10	0.997	81.25	0.999
		Average		1.005		1.009
		Average De	viation	0.006		0.009

(c) <u>Methyl fluorodichloromethane</u> (CH₃CFCl₂)

The photographs showed ten rings and had the visual appearance of the curve marked V, Fig. 14. The radial distribution curve, ED, had peaks at 1.40 Å. (C-F), 1.78 Å. (C-Cl), 2.57 Å. (F···Cl), and 2.87 Å. (Cl···Cl). The exact position of the latter two peaks is probably not too well determined because of the presence of shoulders due to C···F and C···Cl (at about 2.40 and 2.75 respectively) in this region which are not resolved.

In calculating the theoretical intensity curves the same assumptions regarding the C-H terms were made as under methyl fluoroform above. The C-C bond distance was assumed to be 1.54 Å. Theoretical intensity curves and the parameters used in calculating them are shown in Fig. 14. Curve A shows definite disagreement for the tetrahedral model; curves calculated for C-Cl = 1.74 and 1.76 Å. were not any better. Curves B and C correspond to the assumption that the van der Waals repulsion of the methyl group predominates; curves D and E give the methyl group and chlorine atom the same van der Waals radii, the F-C-C and F-C-Cl angles being compressed. Curves F to J were calculated assuming that the repulsion of the chlorine atom affects only the methyl group, the "strain" being taken up In the F-C-Cl angle, which becomes about 108° . Models in the neighborhood of this configuration gave the best agreement with the observed pattern. It is possible that with a shorter C-C distance agreement could also be obtained for slightly

-99-



Figure 14

Methyl Fluorodichloro Methane

Methyl :	Methyl fluorodichloromethane CH3CFCl2					
	C-F	C C1	∠ 01-0-01	<u>/</u> 0-0-01	/ C-C-F	
A	1.38	1.78	109½°	109½°	109½°	
В	1.38	1.78	108	111	111	
C	1.38	1.78	107	112	112	
D	1.40	1.78	111	111	108	
E	1,40	1.78	112	112	107	
F	1.40	1.76	1091	111	109불	
G	1.40	1.76	1091	112	1091	
н	1.40	1.78	1091	111	109날	
I	1.40	1.76	1091	112	108	
J	1.40	1.76	108	112	109]	

For additional curves see R. A. Spurr's Ph.D. Thesis, C.I.T., 1942

TABLE XVI

METHYL FLUORODICHLOROMETHANE

Məx	Min	₫ ₀	q _c (G)	q _c /q _o (G)	q _c (H)	$q_{o}^{\prime}/q_{o}^{\prime}(H)$
٦	1	6.04	6.00	(0.993)	6.10	(1.010)
-	2	12.09	12.60	(1.042)	12.60	(1.024)
2	3	16.11 19.67	16.50 20.20	1.024 1.026	16.40 20.25	1.018
3)	23.84	24.45	1.016	24.40	1.023
4	4	35.26	36.25	1.028	36.40	1.032
5	5	40.14 43.29	40.50 43.70	1.009	40.35	1.005
, ,	6	46.24	46.20	0.999	44.80	0.970
6	7	49.06 53.06	49.60 54.00	1.011	48.80 53.30	0.995 1.005
7	ø	57.31	58.00	1.012	57.50	1.003
g	0	64.09	64.80	1.021	63.60	0.992
9	9	67.74 71.80	68.20 72.25	1.007	67 .10 71.00	0.991
-	10		76.60	-	75.20	-
10		81.80	81.60	0.998	79.80	0.976
	Avera	age	tion	1.013		1.002
	WAARD 1.5	age Devia	1 OII	0.001		0.013

different values of the angle parameters. This possibility was not investigated, since sufficiently good agreement was obtained with the usual value of 1.5^{11} Å. for the C-C bond length. Comparison of calculated and observed q values for models G and H is given in Table XVI. The distances of model H are drawn under the radial distribution curve. The final results are C-F = 1.40 ± 0.03 Å., C-Cl = 1.78 ± 0.03 Å., $\angle C-C-F = 109^{10}_{2} \pm 3^{\circ}$, $\angle C-C-Cl = 111^{\circ} \pm 3^{\circ}$, $\angle Cl-C-Cl = 109^{10}_{2} \pm 3^{\circ}$.

The results for the fluorochloroethanes are summarized in Table XVII below.

TABLE XVII

	CH_CF_3	CH3CF2C1	CH3CFC12	сн ₃ сс1 ₃ (65)
C-F	1.36± 0.02	1.37± 0.03	1.40 ± 0.03	-
0-01	-	1.77±'0.03	1.78 ± 0.03	1.76± 0.02
C C	1.53 ± 0.04	1.54 (assume	ed)1.54(assumed)	1.54 (assumed)
∠ F-C-F	107°± 3°	108°± 5°	-	-
/ C-C-F	112° ± 3°	111°± 5°	109 ¹ 2°± 3°	-
∠ 0-0-01	-	111° ± 5°	111° ± 3°	109°± 2°
/ F-C-Cl	-	108° ± 5°	108° ± 3°	-
/ 01-0-01	-	-	$109\frac{1}{2}^{\circ} \pm 3^{\circ}$	110°± 2°

In these compounds shortening of the C-F distance in the diand trifluoro, but not the monofluoro compound is observed, in agreement with the results of Brockway on the fluorochloromethanes (23). The shortening is doubtless to be ascribed to resonance of the normal covalent structure with ionic structures of the type



which cannot occur with structures containing only one fluorine atom. There is no evidence for shortening of the C-Cl bond length in these molecules; the indication is rather that they are very nearly normal.

(d) dl- and meso-2,3-Dichlorobutane.

This investigation was undertaken in the hope that dl- and meso-2,3-dichlorobutane would yield more definite information on the relative orientations of the methyl halide groups about the 2,3 carboncarbon single bond than had the 2,3-dibromobutanes previously studied by Stevenson and Schomaker (65). The meso- and dl-compounds react with potassium iodide at different rates, with different heats of activation, and their physical constants are quite different (66). It was thought that these effects might result from detectable differences in the relative orientations of the "isopropyl halide" groups about the 2,3 carbon-carbon single bond. No differentiation could be made in the case of the bromo-compounds (65), both of which proved to be essentially trans with respect to the bromine atoms. Although resolution of the problem by electron diffraction should be more likely to be favorable in the case of the chloro-compounds, it was found that it is very probable that there is no essential difference in orientation of the chlorine atoms relative to each other in meso- and dl-dichlorobutane. Only the photographs of the dl-compound were investigated in detail.

Experimental. The meso- and dl-dichlorobutane samples were portions of material prepared in the course of another investigation (67) and were very pure. (Physical constants: <u>meso</u>, b.p. 113.1°C.(746mm), n_D^{25} 1.4409, d²⁵ 1.1023, e²⁵ 6.245; <u>dl</u>, b.p. 117.1 (746mm), n_D^{25} 1.4386,

-105-
d^{25} 1.1063, ϵ^{25} 5.753.) The wavelength of the electrons, determined from transmission photographs of gold foil, was 0.0615 Å., and the camera distance was 10.89 cm. Photographs were made with the liquid at about 50°C. in the starage bulb attached to the electron diffraction apparatus.

Interpretation. The photographs of each molecule showed thirteen rings, and had only slight qualitative differences. Quantitative measurements of the ring diameters, made by three observers, were nearly identical. The visual appearance of the dl-compound photographs is shown by curve V of Figure 15. The characteristic features on the basis of which best agreement with the theoretical curves was decided were: the fourth minimum, which was deeper than the third, the asymmetric ninth maximum, the seventh minimum, which was deeper than the eighth, and the tripled tenth, eleventh, and twelfth maxima. The last named feature was never satisfactorily reproduced in the theoretical curves, although owing to its complicated nature its exact appearance is difficult to determine. Only one radial distribution curve was calculated, that from the measurements of the photographs of the dl-molecule, since with the available data the meso measurements would give the same result within the limits of error of the method. The radial distribution curve, marked RD in Figure 15, shows peaks at 1.05 Å. (C-H), 1.54 Å. (C-C), 1.79 Å. (C-C1), 2.32 Å. (C··H and C1··H), 2.72 Å. (C..C and C..Cl), 3.22 Å., and 4.33 Å. (Cl. Cl). The three longest distances can be accounted for in several ways. The distance

-106-

4.33 Å. corresponds to the longest possible chlorine-chlorine interaction, namely that for a trans arrangement of the chlorines relative to each other, and cannot be accounted for in any other way. With this arrangement the 3.22 A. distance would be due to non-bonded carbon-carbon and carbon-chlorine interactions. The 2.72 Å. distance is the average of C--C and C--Cl (separated by one carbon atom) distances which do not depend on rotation about the 2,3 carbon-carbon single bond. With the values of C-C and C-Cl given by the radial distribution function the calculated C-C-Cl angle is 109°20'. The peak at 3.22 Å. can also be accounted for by a model in which the methyl groups are trans, or one in which the 2,3-hydrogen atoms are trans. In both cases the calculated C1--C1 distance is about 3.20 Å. The corresponding 1,4 C--C distances are at about 3.85 and 2.95 Å. respectively. Thus although most of the scattering is apparently due to molecules in which the chlorine atoms are trans, the radial distribution function cannot exclude the possibility that other rotational isomers are present in moderate amounts, and indeed the shoulder on the curve at about 3.85 Å. suggests that some of these isomers may be present.

The theoretical intensity curves were calculated for the dl-form using the simplified formula

$$I(q) = \sum_{i}^{l} \sum_{j}^{l} \frac{(z_{i} - F_{i})(z_{j} - F_{j})}{(z_{c} - F_{c})^{2}} \sin\left(\frac{\pi}{10} r_{ij}q\right) e^{-a_{ij}q^{2}}$$

$$i \neq j$$

and the atomic scattering factors of Pauling and Sherman (3). The C-H distance was assumed to be 1.09 A., and the temperature factor

coefficient a_{i1} = 0.00015 for bonded C-H terms, and 0.00030-0.00045 for non-bonded C--H and Cl--H terms, and zero for all others. About forty theoretical intensity curves were calculated with C-C distances varying from 1.50 to 1.57 Å., and C-Cl distance from 1.72 to 1.80 Å., the angles C-C-Cl and C-C-C varyng from 109° to 112°, for various orientations of the "isopropyl chloride" groups relative to each other. The angle O between the planes of the C-C-Cl groups is defined by the configuration Cl



looking along the 2,3 C-C axis. The three probable orientations indicated by the radial distribution function, namely, with the chlorines trans, the methyl groups trans, and the 2,3-hydrogens trans, correspond to $Q = 180^{\circ}$, 300° , and 60° respectively. It was found that among the curves calculated for models with a single value of Θ , only those in the neighborhood of 180° gave reasonable agreement with the observed pattern. Some of the theoretical curves and their related parameters are shown in Figure 15. Curve A was calculated omitting terms dependent on rotation, and shows the general pattern to be expected if the molecule had free internal rotation. Curves B and C were calculated for Cl--Cl nearly trans, omitting the long CH₃--Cl terms, which approximates the appearance expected if there is a relatively large amplitude of libration about the trans orientation



Figure 15

d1-2,3-Dichlorobutane

-110-

Legend For Figure 15.

dl-2,3-Dichlorobutane

Curve	0-0	0-01	<u>/</u> c-c-c	<u>∕</u> 0-c-01	θ		
A BCDEFGHIJ	1.54 A 1.54 1.53 1.54 " " " " "	1.76 Å 1.76 1.76 1.76 " " " 1.76	109 ¹⁰ 110 ¹ / ₂ 109 ¹ / ₂	109 ¹⁰ 109 ¹ /2 109 ¹ /2 109 ¹ /2 109 ¹ /2 100 ¹ /2 109 ¹ /2 109 ¹ /2	175° 205 200 180 175 170 170 165 60		
K	H	п	n	11	290	701	
L	n	n	u	tt :	(200 285	70% 30%	L

Table XVIII

d1-2,3-DICHLOROBUTANE

Max	Min	$q_0(meso)$	q _o (dl)	q _c (H)	q _c /q _o (H)
ŀ	1	5•33 9•20	5.02 9.11	6.50 9.40	(1.294) (1.032)
	2	12.00	12.28	12.30	1.002
2		15.46	15.46	15.55	1.005
	3	16.85	16.81	16.75	(0.996)
3		18.46	18.46	19.25	(1.042)
	4	20.85	20.91	21.20	1.013
4	-	24.33	24.27	24.70	1.017
-	5	26.36	27.01	27.80	(1.029)
5	/	29.73	29.85	29.75	(0.997)
(6	51.59	51.55	31.25	(0.997)
0	7	22.00 ZE //12	22.00 25 ZZ	22.0U	(0.996)
7	1	38 58	38 30	38 50	1 003
1	8	41 31	41 b 1	41 90	1.012
8	U	47.19	46.79	46.50	0.994
Ŭ	9	49.33	49.94	49.90	0,999
9	-	52.50	53.00	52.50	(0.991)
	10	54.40	54.35	54.85	(1.009)
10		56.63	56.68	57.80	(1.019)
	11	58.30	58.10	59.25	(1.020)
11		60.45	60.20	60.50	(1.005)
	12	63.67	63.55	64.10	1.009
12		68.25	69.10	69.50	1.006
	13	73.83	74.33	73.50	0.989
13		-	81.68	82.20	1.006
			Average		1.004

Average Deviation 0.005

of the chlorines. Curves D to I were calculated with all terms included, for orientations near 180° . Curves J and K are for H--H trans and OH_{3} -- OH_{3} trans respectively. Curves G (tetrahedral angles) and H ($\angle O-C-C = 109^{\circ}28^{\circ}$, $\angle O-C-Cl = 110^{\circ}30^{\circ}$) gave the best agreement with the observed pattern. For these curves $\theta = 170^{\circ}$, the chlorines being about 10° from the trans position. The distances and angles cannot be fixed very closely, since a change in angle can be compensated by a suitable change in distance, and vica versa. From the appearance of curves B and C and that of the best models G and H it appears that a satisfactory curve with a relatively small amplitude of libration about the trans position could be found, corresponding to a moderately large potential barrier to internal rotation.

The possibility that the observed pattern could be accounted for by a mixture of rotational isomers (as suggested by the radial distribution function) was investigated by adding various percentages of curves for other models to the curve for the chlorines in the trans position. The chlorines-trans molecule must of course be present in large proportion. Mixtures up to about 20% of molecules in other orientations than chlorines-trans do not give curves in marked disagreement with the observed pattern. For higher percentages, the regions of the second and third, and fifth and sixth maxima became wrong, as well as the region of the tripled maxima ten to twelve. Curve L, for a mixture with 30% molecules with $\theta = 285^{\circ}$ and 70% with $\theta = 200^{\circ}$ gave the best agreement obtained for any mixtures having less than 80% of curve H.

-112-

It can be seen that Curve L is not entirely satisfactory in the regions mentioned. It may be concluded that the observed pattern can be satisfactorily accounted for by a model in which the chlorine atoms are nearly trans, perhaps with a moderate amount of libration, or by a mixture including besides the chlorines-trans molecules not more than about 25% of the methyls-trans or hydrogens-trans isomers.

Quantitative comparison of observed and calculated q values for model H are shown in Table XVIII for the dl- compound. Observed q values for the meso form are also given, although these cannot be compared with model H. A model calculated for the meso form with $\theta = 170^{\circ}$, corresponding to a chlorines-trans model with a moderate temperature factor gives reasonable agreement with the observed pattern, so that there can be little doubt that there is no essential difference in the relative orientations of the chlorine atoms in the two molecules. The final results for the dl compound are: $Cl--Cl = 4.33 \pm 0.03$ Å., C-C = 1.55 Å. (assumed), C-Cl = 1.77 Å. (assumed), with angles $C-C-C = 109\frac{10}{8}$ and $C-C-Cl = 110\frac{10}{8}$ (assumed). For the meso compound there is no doubt that the chlorine atoms are also trans relative to each other.

References. Part I.

- 1. L. O. Brockway, Rev. Modern Phys. 8, 231 (1936)
- 2. R. A. Spurr and L. Pauling, J. Chem. Ed. 18, 458 (1941)
- R. W. James and G. W. Brindley, Zeits. f. Krist. <u>78</u>, 370 (1931)
 L. Pauling and J. Sherman, Zeits. f. Krist., 81, 28 (1932)
- 4. L. Bewilogua, Phys. Zeits., 32, 740 (1931)
- 5. R. W. James, Phys. Zeits., 33, 737 (1932)
- 6. L. Pauling and L. O. Brockway, J. Chem. Phys. 2, 867 (1934)
- 7. R. Wierl, Ann. d. Physik, 8, 521 (1931)
- 8. L. Pauling and L. O. Brockway, J. A. C. S. 57, 2684 (1935)
- V. Schomaker, Ph. D. Thesis, Calif. Inst. of Tech., 1938.
 J. Waser, Ph. D. Thesis, Calif. Inst. of Tech., 1944.
- D. P. Stevenson, H. D. Burnham, and V. Schomaker, J.A.C.S.
 61, 2922 (1939)
 - D. P. Stevenson and V. Schomaker, ibid., 62, 1913 (1940)
 - R. Spitzer, W. J. Howell, jr., and V. Schomaker, ibid, 64, 62 (1942)
 - R. Spurr and V. Schomaker, <u>ibid.</u>, <u>64</u>, 2693 (1942)
 - P. Giguere and V. Schomaker, ibid., 65, 2027 (1943)
 - J. Donohue, G. L. Humphrey, and V. Schomaker, ibid., 67, 332 (1945)
- 11. C.-S. Lu and E. Malmberg, Rev. Sci. Inst. 14, 271 (1943)
- 12. P. A. Schaffer, Jr., Ph. D. Thesis, Calif. Inst. of Tech. 1942.
- 13. R. Wierl, Ann. d. Physik <u>13</u>, 453 (1932)
- 14. P. G. Ackermann and J. E. Mayer, J. Chem. Phys. 4, 377 (1936)
- 15. L. E. Sutton and L. O. Brockway, J. A. C. S. <u>57</u>, 473 (1935)

C. D. Carpenter and L. C. Brockway, J. A. C. S. 58, 1270 (1936)

-114-

- 17. V. Schomaker and L. Pauling, ibid., 61, 1769 (1939)
- 17. V. Schomaker and L. Pauling, <u>ibid</u>., <u>61</u>, 1769 (1939)
- 18. Beilstein, "Handbuch der organischen Chemie", 4th Ed. Bd. XVII p. 6.
- 19. A. Verley, Bull. soc. chim. 21, 275 (1899)

16.

- 20. E. L. Buhle, A. M. Moore, and F.Y. Wiselogle, J. A. C. S. 65, 29 (1943)
- 21. L. O. Brockway and K. J. Palmer, J. A. C. S. 59, 2181 (1937)
- 22. C. F. Moerman, Rec. Trav. Chim. de Pays-Bas 56, 161 (1937)
- 23. L. O. Brockway, J. Phys. Chem. 41, 185, 747 (1937)
- 24. L. Pauling and C. D. Carpenter, J. A. C. S. 58, 1274 (1936)
- 25. C. S. Lu, V. Schomaker, et al., to be published shortly.
- 26. E. F. Hatt and E. F. H. Stephenson, J. A. C. S. 65, 1785 (1943)
- 27. S. Karrer and O. R. Wulf, J. A. C. S. 44, 2391 (1922)
- 28. P. Lame, Compt. rend. 198, 918 (1934)
- 29. W. G. Penney and G. B. B. M. Sutherland, Proc. Roy. Soc. <u>A156</u>, 654, 578 (1936)
- 30. The values of this function for O₂ were calculated by Dr. D. R. V. Golding using the data of G. Herzberg, <u>Molecular Spectra</u> <u>and Molecular Structure I</u>, Prentice Hall, N.Y. 1939. The physical constants are those of R. Birge, Rev. Modern Phys. <u>13</u>, 235 (1941). For the method of calculation see E. B. Wilson, jr., Chem. Rev. <u>27</u>, 32 (1940).
- 31. H. A. Stuart, "Molekulstruktur", J. Springer, Berlin, 1934.
- 32. R. S. Mulliken, Rev. Modern. Phys. 14, 204 (1942)
- 33. G. Hetther, R. Pohlmann, and H. J. Schumacher, Z. Elektrochem. <u>41</u>, 524 (1933)

- 34. P. A. Giguere and V. Schomaker, J. A. C. S. 65, 2025 (1943)
- 35. L. Pauling, "The Nature of the Chemical Bond", p. 164. Cornell University Press, 1940.
- 36. L. Pauling, ibid., p. 195.
- 37. C. P. Smyth and G. L. Lewis, J. A. C. S. 61, 3063 (1939)
- 38. A. Baeyer and V. Villiger, Berichte <u>33</u>, 3387 (1900)
 R. Willstätter and E. Hauenstein, Berichte <u>42</u>, 1842 (1909)
 A. Rieche, "Alkylperoxyde und Ozonide", Th. Steinkopf, Dresden, 1931.
- 39. L. R. Zumwalt and P. Giguere, J. Chem. Phys 9, 458 (1941)
- 40. S. Vankateswaran, Phil Mag. vii 15, 263 (1933)
- 41. W. Theilacker, Z. physik. Chem. B20, 142 (1933)
- 42. W. G. Penney and G. B. B. M. Sutherland, Trans. Farad. Soc. <u>30</u>, 898 (1934); J. Chem. Phys. <u>2</u>, 492 (1934)
- 43. C.-S. Lu, E. W. Hughes, and P. A. Giguere, J.A.C.S. 63, 1507 (1941)
- 44. K. J. Palmer, J. A. C. S. 60, 2360 (1938)
- 45. O. Ruff and W. Menzel, Z. anorg. Chem. <u>211</u>, 204 (1933)
 P. Firsch and H. J. Schumacher, Z. physik. Chem. <u>B24</u>, 322 (1936);
 B37, 1, 25 (1937); Z. anorg. Chem. 229, 423 (1936).
- 46. A. Rieche, Berichte 61, 951 (1928)
- 47. For extensive bibliographies see the review articles by
 - (a) L. Long, Chem. Rev. 27, 437 (1940)
 - (b) A. Rieche, R. Meister, and H. Sauthoff, Annalen 553, 288 (1942)
- 48. E. Erdmann, J. prakt. Chem. (2) 85, 78 (1912)
- 49. E. Briner and S. de Nemitz, Helv. Chim. Acta 21, 748 (1938)
- 50. C. D. Harries, Annalen 374, 288 (1910)
- 51. H. Staudinger, Berichte 58, 1088 (1925)

- 52. W. Traube and E. Lehmann, Berichte 32, 720 (1899)
- 53. E. Briner, K. Ryffel, and S. de Nemitz, Helv. Chim. Acta 21, 357 (1938)
- 54. L. Pauling, "The Nature of the Chemical Bond", pp. 62, 131.
 2nd Ed. Cornell University Press. Ithaca, N. Y. 1940.
- 55. L. Kassel, J. Chem. Phys. 1, 414 (1933)
- 56. C. M. Anderson and E. C. Gilbert, J. A. C. S. <u>64</u>, 2369 (1942)
- 57. O. Westphal and M. Eucken, Berichte 76B, 1137 (1943)
- 58. C. D. Harries and R. Koetschau, Berichte 42, 3305 (1909)
- 59. C. D. Harries and F. Evers, Annalen 390, 238 (1912)
- 60.. The trans-2-butene was obtained from Dr. R. Rasmussen of the Shell Development Co, and analysed 86% trans-2-butene, 12 % cis-2-butene, 1% 1-butene, and 1% n-butane.
- 61. V. Schomaker and L. Pauling, J.A.C.S. 61, 1769 (1939)
- 62. G. Glockler, Rev. Modern Phys. 15, 151 (1943)
- 63. H. Russell, D. R. V. Golding, and D. M. Yost, J.A.C.S. <u>66</u>, 16 (1944)
- 64. J. Y. Beach and D. P. Stevenson, J.A.C.S. 61, 2643 (1939)
- 65. D. P. Stevenson and V. Schomaker, J.A.C.S. <u>619</u> 3173 (1939)
- 66. R. T. Dillon, W. G. Young, and H. J. Lucas, J.A.C.S. <u>52</u>, 1953 (1930)
- 67. H. J. Lucas and C. W. Gould, jr., J.A.C.S. <u>63</u>, 2541 (1941)

Part II

•

.

On the Ultraviolet Absorption Spectrum

of Ozone

On the Ultraviolet Absorption Spectrum of Ozone

A number of attempts have been made to deduce the configuration of the ozone molecule from the available experimental data on the infrared absorption spectrum of ozone. However, the infrared absorption spectrum of ozone has not been examined in sufficient detail under high enough dispersion to allow an unambiguous assignment of the three fundamental vibration frequencies, and the present possible assignments remain doubtful. The spectroscopic evidence on the structure of ozone has been critically reviewed recently by Simpson (1), who gives a new assignment of the fundamental frequencies. The experimental data are summarized in Table I. The Raman spectrum of ozone has not yet been obtained owing to the strong absorption of ozone in the region generally used in Raman work (2).

Table I

Obs Frequ	erved encies	, cm^{-1}	In- tens	Envel. . Type	Frequency	Assignment*		e
HPS	G	A			HPS	PS	A	S
695 725 1037 1740 2105 2800 3050	710 1033 1055 2108	1043	8 V 8 W 8 W W	Doublet ? Q? ? ?		24; ; 342 24; ; 342 24; + 42 34;	¹ √2 1/1 1/1 + 1/2 1/3 2.4/1 + 1/2 3.4/1 3.4/1	ℓ- [−] ℓ ₂ [−] K [−] ℓ ₁ [−] [−] K [−] K ⁺ [−] K ² [−] K ⁺⁺ [−] K ² [−] K ⁺⁺ [−] K ² [−] K ²

HPS = Hettner, Pohlmann, Schumacher (3), PS = Penney and Sutherland (6), G = Gerhard (4), A = Adel (5).

* $\boldsymbol{\mathcal{V}}_1$ is essentially the symmetrical stretching frequency, $\boldsymbol{\mathcal{V}}_2$ the symmetrical bending frequency, and $\boldsymbol{\mathcal{V}}_2$ the asymmetrical stretching frequency

-118-

The fact that at least two independent frequencies appear in the infrared, and that binary combinations of active bands seem to occur, rules out an equilateral triangle structure of ozone, or a linear molecule (7). A completely unsymmetrical structure seems very unlikely, and only an isosceles triangle remains to be considered. The electron diffraction results presented in Part I show that ozone has an obtuse angled isosceles triangle structure with apical angle 127° and bond length 1.26 Å. If the electron diffraction results are accepted, then from the moments of inertia of the molecule and the calculations of Nielsen (8) on the band types of slightly asymmetrical top molecules it can be predicted that the \mathbf{P}_{Z} band should have a Q-branch and that the $\boldsymbol{\mathcal{V}}_1$ and $\boldsymbol{\mathcal{\mathcal{V}}}_2$ fundamentals should show doublet structure. On this basis only the Penney-Sutherland, Adel, and Simpson assignments are acceptable. Simpson (1) has carried out valence force field normal coordinate treatments for the four proposed assignments, with the results shown in Table II.

Table II

	7,	¥2	P3	f	dl	d_2	Angle	0-0,Å·	$C_p(calc)$
S HPS PS A	1740 2105 1043 1043	1043 1043 710 710	2105 710 1740 2105	15.98 1.82 10.91 15,98	3.023 38.90 0.735 0.503	3.12 11.26 _	125 ⁰ 33 164 i	1.17 1.69 1.23 1.17	8.86 9.80 9.89 9.80

f = 0-0 stretching constant x 10^{-5} dynes/cm. d₁= 0-0-0 bending constant x $10^{-5}/r^2$ dynes/cm/ d₂= stretching-bending interaction constant x 10^{-5} dynes/cm. C_p (observed) = 10.94 at 400°K.

-119-

For comparison with the constants in Table II there are given in Table III the 0-0 frequencies (to be compared with ψ_1), 0-0 bond lengths, and 0-0 stretching force constants for hydrogen peroxide, oxygen, and ozone. The force constant for ozone was calculated from Badger's Rule (10) and the electron diffraction result for the 0-0 bond length.

	Ta	ble III	
	v cm ⁻¹	0-0 Å.	f x 10^{-5} dynes/cm.
H ₂ 0 ₂ (11)	875	1.47	3 •7
0 ₃	-	1.26	9•5
Ø2 (12)	1550	1.208	11.3

From Table II it can be seen that the Hettner-Pohlmann-Schumacher assignment gives very unlikely values of the force constants, interatomic distance, and angle, in addition to giving the wrong contours to the bands; this assignment can probably be rejected. The Penney-Sutherland assignment gives the most reasonable values of the force constants, but a rather large angle. It would also make the 1740 cm⁻¹ fundamental much weaker than the overtone at 2105 cm⁻¹, which is unusual. The Adel assignment gives an imaginary angle and a large force constant. The Simpson assignment gives large force constants and makes the difference frequency (η - η) much stronger than the fundamental \mathcal{P}_{η} . None of these assignments gives good agreement with the observed heat capacity, which would require at least one of the frequencies to be rather low. This suggests that the observed heat capacity, which was determined from

explosion data (9), may be in error, since no bands have been observed in the infrared region between 300 and 700 cm⁻¹(3). A more detailed analysis of the infrared absorption bands will be required before any of the assignments given above can be considered reliable. A determination of the types of the envelopes of the 1740 and 2105 cm⁻¹ bands would be desireable, as well as a study of the temperature dependence of the 710 and 1740 cm⁻¹ bands. In view of the uncertainty in the interpretation of the infrared data, it was thought that additional data might be obtained from the ultraviolet absorption spectrum of ozone, which as yet has only been incompletely analysed. In particular, an analysis of the effect of change of temperature on the vibrational structure of the band system in the ozone spectrum lying in the region 3000-3850 R. offers hope of affording additional information as to the fundamental vibration frequencies of the normal state of the molecule. Such an analysis involves the finding and interpretation of a number of bands, among the many members of the system, which originate in transitions from excited vibrational levels in the normal electronic state of the molecule. It should be possible to identify these bands by the pronounced increase with temperature of the intensity of their absorption.

The absorption spectrum of ozone in the region from 3000-3650 Å. (13-18) consists of a system of diffuse bands falling off rapidly in intensity with increasing wavelength which appear to overlie a background of continuous absorption. The intense bands in this region

-121-

may be ordered in groups of partial progressions and interpreted in terms of transitions from a vibrationless ground state to an upper electronic state in which two vibrational frequencies are excited. A formula for these which has been suggested by Jakowlewa and Kondratjew (17) seems to fit the positions of the bands reasonably well:

$$\boldsymbol{\nu} = 28447 + 636.7 v_1^{1} - 16.0 v_1^{2} + 351.7 v_2^{1} - 4.5 v_2^{12} - 0.17 v_2^{13}$$

-12.0 v_1^{1} v_2^{1} - 1.5 v_2^{1} v_1^{2} - 0.5 v_1^{1} v_2^{12} - 1058 v^{n} + 11.5 v^{n}^{2}

In addition to the bands described by this expression there exists, principally to longer wavelengths, a large number of weaker bands. These bands are strongly temperature-sensitive and may presumably be ascribed to transitions from excited vibrational levels in the ground state. If this is the case it is to be expected that these bands may be ordered in such a way as to form progressions homologous to the temperature-insensitive bands but shifted toward the red from them by constant frequency differences corresponding to the energies of the excited vibrational levels of the ground state. Four bands of such a group, based upon the frequency 1043 cm.¹, have been observed in work at the temperature -78°C., room temperature, and 100°C. (16,17) With the present work the attempt has been made to extend the ultraviolet absorption spectrum of ozone to longer wavelengths in order to obtain more data on the temperature-sensitive bands, to ascertain that no temperature-insensitive bands lie beyond the proposed (000)" \rightarrow (000)' band (14,17) at 3514 $\hat{\mathbf{x}}$, and to classify as many as possible of the temperature sensitive bands in terms of vibrational frequencies of the

-122-

ground state as indicated by observations in the infrared.

The absorption was studied at room temperature and at 90° C. in the region of weak absorption from 3439 to 3850 $\stackrel{\rm O}{\rm A}$. by means of a Bausch and Lomb Littrow quartz spectrograph with a dispersion of about 7 Å. per millimeter in this region. A 500-watt tungsten projection lamp was used as a light source. The absorption cell was an 8-meter glass tube enclosed in a stainless steel jacketing tube which could be heated electrically. The ozone was prepared by passing a continuous stream of tank oxygen through two Siemens type ozonizers and then through the cell. Dry-ice traps were provided to condense N205, which catalyses the decomposition of ozone at the higher temperature, and might contribute to the absorption in this region if its partial pressure were not kept sufficiently low (19). The concentration of ozone in the cell was estimated by means of the absorption coefficients of Ny and Choong (20) at 3439 $\stackrel{\circ}{\mathbf{A}}$. to be about 6%. The positions and relative intensities of the bands were determined from microphotometer traces; the weakness of the bands and the intensity of the continuous background made measurements with a visual comparator impractical. A large number of bands was observed, including all of those indicated by Chalonge and Lefebvre (15), and other bands at longer wavelengths. In all, seventyfour bands were recorded, although some of these were very weak, and longer ozone paths or higher concentrations would be necessary to confirm their existence and to determine their exact positions. The

-123-

positions of the bands could be estimated to an accuracy of only about ± 1 Å. in the region 3439 to 3600 Å., and ± 2 Å. in the region 3600 to 3850 Å.

An approximate estimate of the absorption coefficients of the bands was made using the optical density of the photographic plate as indicated by the photometer traces and the Hurter and Driffield curves for the plate. The ratio of these calculated coefficients at the two temperatures 90°C. and 25° C. was used as an indication of the temperature sensitivity of the bands. It was found that the ratics of the absorption coefficients at the two temperatures for bands assigned to transitions of the type (000)" \rightarrow (v_1v_20) ' were considerably less than those for bands believed due to transitions from excited vibrational levels in the lower electronic state. That the "temperature-insensitive" bands vary at all with temperature is probably due to overlapping of portions of adjacent temperature-sensitive bands. In particular, of all the bands here studied, only those at 3439, 3472, and 3514 Å. were relatively insensitive to temperature change; all other bands in this spectral region increased more rapidly in intensity on heating than these. Thus, the data seem to confirm quite well the assignment of the band at 3514 Å. to the transition (000)" \rightarrow (000)'.

An attempt was made to classify the remaining temperature-sensitive bands in the following fashion. The intense bands previously reported (14-17) and arranged in an array of partial progressions were assumed to be due to transitions from the vibrationless ground state. (A con-

-124-

venient tabulation of these bands is given by Melcher, reference 18) Energies corresponding to assumed vibrational levels were subtracted from the energies associated with these temperature-insensitive bands, and the tabulated data were searched for bands with frequencies corresponding to those calculated by this method. Because of the diffuse character of the bands, the accuracy of the measurements limited the precision obtainable in matching the calculated and observed frequencies, and agreement to within about 15 cm⁻¹ was considered acceptable. Attempts were made to classify the bands in terms of the assumed fundamental frequencies 710, 1043, 1740, and 2105 cm⁻¹, which appear as reasonable possibilities in the light of previous investigations of both the infrared and ultraviolet spectrum of ozone (1,21).

Table I summarizes the positions of the bands observed and the transitions assigned to them. Only two frequencies were employed in the upper state, according to the expression above, since the data did not seem to justify the assumption of a third. Because of the lack of resolution, the two frequencies 1740 cm^{-1} , assumed as a possible fundamental, and 1753 cm^{-1} , corresponding to $(710 \pm 1043) \text{ cm}^{-1}$, are tabulated together; the data do not allow of a distinction between these two possibilities.

Table II was prepared to show the comparative number of bands which can be fitted by the various assumed combinations of fundamental frequencies. The columns of the table give the number of bands in Table I which are accounted for by schemes based on the lower-state vibrational frequency shown at the head of the respective column. The last row gives the maximum number of bands which are fitted by each frequency regardless of whether it is possible to account for some of

-125-

these bands by others of these frequencies. The remaining rows give the number of bands which may be described, without duplication, by the groups of frequencies listed in the left-hand column, providing the counting is done in the following manner. Bands which can be accounted for by the first listed frequency are tabulated in the column allocated to this frequency; then bands not already accounted for by the first frequency, but given independently by the second frequency are counted and entered in the corresponding frequency column, and similarly for the third frequency excluding bands ascribed to the first and second. Finally bands accounted for by combinations or other frequencies are listed in their respective columns, but also always in such a way that no band is counted more than once. In the tabulation, bands arising from the vibrationless ground state have been omitted. Not all of the bands which are listed in Table I have been fitted into any of the schemes of Table II; twelve bands are not accounted for by any transitions based on the frequencies assumed. These hands are almost all at the long wavelength end of the band system and are very weak. Uncertainties in the measurement of their positions are large, and they may actually be spurious. It is, however, not unreasonable to suppose that they may arise from still higher levels in the ground state than have been employed in the calculations, and it is believed probable that these bands could be accounted for satisfactorily in that fashion. In addition, it should be pointed out that no value for ${m \nu}_3'$ has been suggested, and it might

-126-

indeed be profitable to examine the positions of the unassigned bands for such a possibility. It is interesting that in a study by Clements (22) of the effect of temperature on the ultraviolet absorption spectrum of the similar molecule sulfur dioxide no indication of the γ_{j}^{1} or γ_{z}^{n} frequencies was found.

It will be noticed that the frequency 1043 cm⁻¹ enters into all of the assumed schemes. The assumption of this frequency as a fundamental seems hardly disputable since the intensity of the bands arising from transitions based upon this frequency is greater by far than any other band arising from transitions of a similar type. The infrared data (1) are also in support of this frequency as a fundamental. Transitions arising from levels of this set but higher than the first were fitted by adjusting the first anharmonic term in the expansion of the energy of the vibrational state so as to give as accurate a fit as possible to the positions of temperature dependent bands in the correct neighborhood. With both this frequency and that based on 710 cm⁻¹ only the square term in the expansion is given, since it is not believed that the three infrared frequencies involved in the bands associated with the 1043 cm.¹ separation and the four infrared frequencies involved in the bands associated with the 710 cm⁻¹ separation justify the addition of higher terms. The energy (expressed in wave numbers) corresponding to higher levels of these two vibrations fitted in the way described are represented by the following two formulas:

 $\boldsymbol{\nu}_{1}^{"} = 1066 v_{1}^{"} - 23 v_{1}^{"}^{2}$ $\boldsymbol{\nu}_{2}^{"} = ,727 v_{2}^{"} - 17 v_{2}^{"}^{2}$

The point to which particular attention is called is demonstrated by Table II, namely, that it is possible to ascribe almost all of the bands observed in the temperature-sensitive untraviolet spectrum of ozone to the two fundamental frequencies 710 and 1043 cm⁻¹, and their harmonics and combinations. Some bands fit into schemes in which other fundamental frequencies are assumed, but these bands are just as well classified by the first two frequencies, which explain many other bands in addition. Moreover, the assumption of frequencies for the ground electronic state which do not include 710 cm. results in a scheme which is considerably inferior in classifying all the bands. It accordingly seems very unlikely that 710 cm⁻¹ can be eliminated as one of the fundamental frequencies of the ozone molecule. On this basis the Simpson assignment of the fundamental frequencies must be considered unlikely, and only the Penney-Sutherland and Adel assignments seem to be acceptable. Until a detailed study of the infrared absorption spectrum is made, however, no further conclusions regarding the structure of ozone based on the available spectroscopic data seem justifiable.

assignments	
possible	
their	2
Bnd	
observed	
bands	
the	9
of	
Summary	

	$(0^{z}_{i}\Lambda^{T}_{i}\Lambda)$	"(0 Z T) "()	24 A1 A1	l									4					63 69		C V
	(⁴ ¹ ⁴ ⁰	0 1 1)	А - Г А											ର ର		0 0				
	(0 ² A	(" AO	0 P								0									
ຄ	, ∧)	0)	•								4									
73= 210			ч З З								Ч									
~	()	â	-07	6	N	0	2			Ч	5	Ч	3				N	0	~	
"= 710	(V1 V2)"A 0)			-	હ	જ			Ч	Ч	જ	~				0	Ч	Ч	
P	-		# 62 A		H	Ч	~			Ч	2	2	ю				Ч	Ч	હ્ય	
1043	(0	()	- 03	0	5	Ч		Ч		~	0				З	0	ы	Ч		
11	141	0	 	r-I	-	2		0		щ	~				4	0	0	Ч		
r	Δ)	<u>></u>	"	0	r-i	Ч		0		Ч	Ч				З	0	Ч	Ч		
	State	State	Oras o	1.07	1.25	1.24	1.22	1.16	1.34	1.48	1.40	1.43	1.53	1.48	1.50	1.23	1.37	1.44	1.44	
	pper	ower		cm ⁻¹																
	p	н		29070	28994	28927	28868	28794	28719	28679	28604	28580	28547	28514	28490	28442	28417	28353	28329	
				O-T																
			Band	3439	3448 3452	3456	3463	3472	3481	3486	3495	3498	3502	3506	3509	3514	3518	3526	3529	

Table I

	Ľ.) 1						a		0				. 1			3		Ч							~		0			
	0	1 63						CV.		60							Ч		Q							Ч		~			
	Ч				2		0						Ю			Ч						2		-	0						
	હ્ય				Ч		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~						0			Ч						0									
		0															0														
		Ю															2														
2		ч															Ч														
inued	~2	ю.н	Ч		ы	Ч				ດ 3	0		0	હ્ય	0		0				Ч		3	Ч	н			١			
(cont	~3	00	Ч		Ч	જા				0	0		Ч	Ч	<u>ര</u>		ю				0		ч	Ч	ณ						
н	63	62 H	~		Ю	ю				2			~	Ю	ы		4				2		4	3	4						
Table	હ્ય	લ્ય	0	ч		Ч			N 2			0		N 3	0	ы			ч		0		н			~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~			0		
-	2	0	Ч	4		2			5	0		4		-+	രു	~			б		0		ч		x.".	~			3		
	~2	Ч	Ч	3		જ			Ю	Ч		ы		N	N3	ы			З		Ч		~			ы			Ю		
	1.59 1.59	1.69	1.47	1.42	1.47	1.53	1.52	1.45	1.40	1.36		1.32	1.34	1.31	1. 36	1.40	1.37	1.47	1.41	1.47	1. 35	1.37	1.33	-	1.35*			1. 36			
	em-1														сē.																
	28256 28201 28137	28082	28027	27995	27964	27925	27902	27847	27801	29749		27724	27708	27662	27616	27586	27563	27541	27518	27487	27405	27381	27352		27337	27285	27262	27225	27211	27196	27181
	04																														
	3538 3545 3553	3560	3567	3571	3575	3580	3583	3590	3596	3603	3606	3606	3608	3614	3620	3624	3627	3630	3633	3637	3648	3651	3655		3657	3664	3667	3672	3674	3676	3678

. 1

-

* At wavelengths greater than 3680 Å. the values given are for the region of the spectrum, since the ratio of absorption coefficients for bands at these wavelengths differed very little from that of the background.

		3		r-1						N 2		0					Ч	0		
		0		- -1						0		r -1					0	0		
		ч								0										
		0								0										
				0												-	0			j
				Ч													0			
				Ч													Ч			
	N N O O	0					Ю	•• 	4						 0 0	N			ч	
	0440	ດາ					ō	ЧС	>						ч0	0			0	
	50 4 10 03	4					4	4 K	2						4 3	4			4	0
	ଷ	o	Ч						Ч	2	0			Ю		HO.			ಷ	
	0	ᆔᆔ	~						0	Ч	~			0		н0			0	,
	~	10 N	Ю						~3	Ю	ю			Ю		50 03	!		ю	3
m-1 1.32*		1.32						1.31									1.33			
27159 c 27144 27107	27093 27071	6107 <i>3</i>	26976	26961	26889	26874	26838	26773	26745	26709	26659	26638	26587	26469	26434	26406	26343	26143	26034	Ĭ
3681 Å. 3683 Å.	3690 3693	3700	3706	3708	3718	3720	3725	3734	3738	3743	3750	3753	3760	3777	3782	3786	3795	3824	3840	

Table I (continued)

Table II

q 400 Wumher of hands fitted into

Number	0 F	bands	fitted	into scheme	of freque	sucy	
Frequencies excited in lower state		043	014	1740 Or	1043 -	2105	Total
Order of use of Frequencies				0T = 0*0T	OT X V		
104 <i>3</i> 710		33	14	4	Ø	0	59
710 1043		D L	32	4	Ø	0	23
1740 1043 710		53	10	12	ß	0	53
2105 1043 710		31	13	4	Q	ຸ	53
2105 1043 1740		31	8	4	8	сл	43
Maximum number		33	32	22 1	Ø	ດາ	

References. Part II.

1. D. Simpson, Trans. Farad. Soc. <u>41</u>, 209 (1945) 2. G. B. B. M. Sutherland and S. L. Gerhard, Nature 130, 241 (1932) 3. G. Hettner, R. Pohlmann, and H. J. Schumacher, Z. Elektrochem. 41, 524 (1933) 4. S. L. Gerhard, Phys. Rev. 42, 622 (1933) 5. A. Adel, Astro. J. <u>89</u>, 320 (1939); <u>94</u>, 451 (1941) A. Adel, V. M. Slipher, and O.Fouts, Phys. Rev. 49, 288 (1936) 6. W. G. Penney and G.B.B.M. Sutherland, Proc. Roy. Soc. A156, 654 (1936) 7. G. Herzberg, "Infrared and Raman Spectra", pp 124, 265, 286. D. Van Nostrand, New York, 1945. 8. H. H. Nielsen, Phys. Rev. <u>43</u>, 197 (1933). 9. B. Lewis and G. von Elbe, J. Chem. Phys. 2, 294 (1934) 10. R. M. Badger, J. Chem. Phys. 2, 128 (1934); 3, 710 (1935). G. Herzberg, loc. cit., p. 301. 11. 12. G. Herzberg, "Molecular Spectra and Molecular Structure I", p. 491. Prentice Hall, New York, 1939. 13. A. Fowler and G. Strutt, Proc. Roy. Soc. 93, 729 (1917) 0. R. Wulf and E. Melvin, Phys. Rev. 38, 330 (1931) 14. D. Chalonge and L. Lefebvre, Comt. rend. 197, 444 (1933) 15. 16. L. Lefebvre, Compt. rend. 199, 456 (1934) 17. A. Jakowlewa and K. Kondratjew, Phys. Zeits. Sowjetunion 9, 106 (1939) 18. D. Melcher, Helv. Phys. Acta 18, 72 (1945)

E. J. Jones and O. R. Wulf, J. Chem. Phys. <u>5</u>, 873 (1937)
 T.-Z. Ny and S.P. Choong, Chinese J. Phys. <u>1</u>, 38 (1933)

21. R. S. Mulliken, Rev. Modern Phys. 14, 204 (1942)

22. J. H. Clements, Phys. Rev. <u>47</u>, 224 (1935)

Summary

The interatomic distances and bond angles in methyl cyclobutene and methylene cyclobutane have been determined. Results on the carbonoxygen cyclic compounds trimethylene oxide, ethylene methylene dioxide, dioxane, and trioxane, and the carbon-nitrogen cyclic compounds pyrazolidine and trimethylene pyrazolidine are summarized in Table VII. The ozone molecule is shown to have the configuration of an obtuse isoceles triangle. The structure of dimethyl peroxide has been investigated. Ethylene ozonide and 2-butene ozonide are shown to be non-planar fivemembered ring structures. Results on the methyl fluorochloromethanes are summarized in Table XVII. meso- and dl-2,5-Dichlorobutane are shown to have essentially trans configurations with respect to the chlorine atoms. Detailed results on each compound will be found at the conclusion of the respective sections.

The effect of change of temperature on the ultraviolet absorption spectrum of ozone in the region 3400 to 3900 Å. has been investigated. The temperature dependent bands are ascribed to transitions from excited vibrational levels in the ground electronic state, and are classified in terms of frequencies observed in the infrared absorption spectrum. It is shown that most of the bands can be accounted for by use of the two fundamental vibration frequencies 710 cm⁻¹ and 1043 cm¹.

-134-

Acknowledgements

I am particularly indebted to Professor Verner Schomaker for instruction and advice in the interpretation of electron diffraction photographs, and his help in all of the electron diffraction investigations. Certain of the compounds were done in collaboration with other investigators, whose assistance is gratefully acknowledged: on ethylene methylene dioxide and dioxane, Dr. W. West; on all of the heterocyclic compounds, Dr. C.-S. Lu; on ozone and the fluorochloroethanes, Dr. R. A. Spurr; on dichlorobutane, Dr. L. Steiner. The work on the ultraviolet absorption spectrum of ozone was done in collaboration with Dr. W. H. Eberhardt, with the advice and assistance of Dr. O. R. Wulf of the U. S. Weather Bureau, and of Professor R. M. Badger. I am also indebted to Professor Linus Pauling for many helpful discussions and suggestions, and for much encouragement in these investigations.