

separated out. A second crystallization from ethanol usually gave crystals melting at 171–172°. The yield of pure *p*-iodonitrobenzene was determined and an estimation of the amount remaining in the solvent was made. For this purpose the solubility in 95% ethanol at 25° was taken as 0.76 g. in 100 cc. of solution. There was also taken into consideration a loss due to a side reaction which liberates iodine. This sometimes was as high as 9%. On this basis, then, the amount of para nitration was calculated to be about 14%.

When the rearranged product was examined from the standpoint of thermal analysis it was first of all shaken up with a dilute solution of sodium thiosulfate. The iodine-free mixture was then extracted with chloroform, the chloroform solution was separated, washed with water, dried and evaporated to dryness. The melting point of the residue was determined and from the tables given by Challenger and Rothstein^{3b} the amount of para nitration was calculated to be 19%. In this work it was assumed that no ortho compound was present,^{3b} and no attempt was made to fractionate the material prior to a melting point determination.

Pure di-*m*-nitrophenyliodonium iodide was treated according to a procedure similar to the above, and no *p*-iodonitrobenzene could be detected.

Some typical experiments are recorded in Tables I and II.

TABLE I

Experiment	I	II
Yield of nitrated iodonium iodide, g.	13.4	14.2
Yield of <i>p</i> -iodonitrobenzene, g.	1.20	1.34
<i>p</i> -Iodonitrobenzene remaining in solvent, g.	0.60	0.45
Loss due to iodine liberation, g.	0.16	0.16
<i>p</i> -Nitration, %	14.6	13.9

TABLE II

Experiment	III	IV
Yield of nitrated iodonium iodide, g.	13.4	13.7
M. p. of rearranged material	88°	89°
<i>p</i> -Nitration, %	18.5	19.0

Summary

Diphenyliodonium nitrate has been nitrated and the work of Challenger and Rothstein, which shows that a considerable amount of para nitration occurs along with meta nitration, has been confirmed.

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The Dipole Moments and Structures of Ozone, Silicobromoform and Dichloroform

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The structures of the molecules of the three inorganic substances, ozone, silicobromoform and dichloroform contain contributions from several forms among which resonance exists. It has seemed desirable to investigate the relation of each of these structures to its dipole moment.

The dipole moments were obtained in the usual manner from the dielectric constants ϵ and the densities d of solutions of the substances in non-polar solvents by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{c_1 M_1 + c_2 M_2}{d}$$

and

$$P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2 , M_1 and M_2 , and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual components, the subscript 2 referring to the polar substance. The values of P_∞ obtained by extrapolating the $P_2 - c_2$ curves to infinite dilution are used to calculate the dipole moment μ by means of the equation

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T}$$

in which MR_D is the molar refraction for the D sodium line and T is the absolute temperature.

Preparation of Materials

Heptane.—Material from the American Petroleum Corporation was used without purification, d^{25}_4 0.67958, n^{25}_D 1.38428.

Carbon Tetrachloride.—Purification of this solvent was carried out by standard methods:¹ d^{25}_4 1.58431, n^{25}_D 1.45717, ϵ^{25} 2.223.

Oxygen.—Tank electrolytic oxygen was passed through concentrated sulfuric acid and over phosphorus pentoxide and condensed by means of liquid air: $d^{-192.5}_4$ 1.1937, $\epsilon^{-192.2}$ 1.505.

Ozone.—A solution of ozone in liquid oxygen was prepared by passing a stream of purified oxygen through an ozonizer and condensing the product directly in the dielectric cell or the pycnometer surrounded by liquid air. The concentration of the solution was determined by allowing the liquid to evaporate through neutral potassium iodide solution in three gas washing bottles in series into a large aspirator bottle. The volume, measured within 0.1%, was then used to determine the total number of moles of oxygen plus ozone; the mole fraction of ozone was determined iodimetrically with sodium thiosulfate.

Silicobromoform.—A pure specimen of silicobromoform was given us by Professor W. C. Schumb of the Massachusetts Institute of Technology.

(1) Williams and Krehma, THIS JOURNAL, 48, 1888 (1926).

Dichlorogermane.—About 1 cc. of dichloromonogermane was prepared by Messrs. S. R. Ginsburg and A. J. Grossman by a method outlined elsewhere.² Because of its instability, the material was not of a high degree of purity. It was kept in a sealed tube under its own pressure immersed in liquid air until the solutions in carbon tetrachloride were made up.

Experimental Methods

The dielectric constants were measured at a frequency of 520 kilocycles with a crystal-controlled heterodyne beat apparatus described elsewhere,³ an accuracy of 0.05% being attained. The densities at 25° were measured with an Ostwald-Sprengel pycnometer. After being suspended in the constant temperature kerosene bath for twenty minutes, the pycnometer was set to the mark in the customary manner, removed from the bath, rinsed with distilled ether, wiped with a clean handkerchief, and weighed. Densities were reproducible to ± 0.00001 . For measurements of the density of liquid oxygen and oxygen solutions of ozone, the pycnometer used was a glass bulb with a very fine capillary opening. The volume of the bulb was determined by weighing full of mercury and was corrected for change with temperature. The weight of the liquid was determined from the volume of gas formed on evaporation just as in the determinations of the concentrations of the solutions. The density of the liquid oxygen could be reproduced to 0.001.

The solutions of silicobromoform and dichlorogermane were made up in an atmosphere of carbon dioxide by the simple device of placing dry-ice on the bottom of a large can, placing a glass-stoppered weighing flask containing a weighed amount of solvent upon a platform just above the dry-ice, holding the tube containing the active substance near the bottom of the can when opening it and immediately adding the active solute to the weighed solvent without removal from the can. Decomposition in the dilute solutions thus prepared was too slow to affect the accuracy of the measurements.

TABLE I
DIELECTRIC CONSTANTS, DENSITIES AND
POLARIZATIONS

ϵ	d	P_2
Oxygen-Ozone ($t = -192.4^\circ$)		
0.00000	1.505	1.1937 (3.86 = P_1)
.00855	1.534	1.1983 26.1
.00950	1.537	1.1989 25.9
.00970	1.537	1.1990 25.4
Heptane-Silicobromoform ($t = 25^\circ$)		
0.00000	1.917	0.67958 (34.49 = P_1)
.05473	1.960	.75500 45.6
.08327	1.982	.79433 45.8
.12972	2.019	.84834 46.3
.16718	2.048	.90996 46.5
Carbon Tetrachloride-Dichlorogermane ($t = 25^\circ$)		
0.00000	2.2282	1.58436 (28.20 = P_1)
.01175	2.3010	1.58651 122.5
.01762	2.3375	1.58747 121.8
.02616	2.3963	1.58895 123.9

(2) Ginsburg, Grossman and Smyth, to be published.
(3) Lewis and Smyth, *J. Chem. Phys.*, **7**, Nov. (1939).

TABLE II
MOLAR REFRACTIONS, POLARIZATIONS AND DIPOLE
MOMENTS

Substance	MR_D	$P_\infty (t^\circ)$	$\mu \times 10^{18}$
O ₃	7.6	26 (-192.4°)	0.49
SiHBr ₂	33	46 (25°)	.79
GeH ₂ Cl ₂	21.8	123 (25°)	2.21

Experimental Results

The dielectric constants, densities and polarizations are given in Table I. Table II lists in the second column molar refractions, calculated from the refractive index of gaseous ozone given by "International Critical Tables," and calculated for silicobromoform from the atomic refractions given by Eisenlohr⁴ and for dichlorogermane from the atomic refractions obtained from Landolt-Börnstein and from the data of Miller.⁵ The succeeding columns give the polarization at infinite dilution P_∞ with the corresponding temperatures in parentheses and the dipole moments.

Discussion of Results

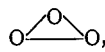
The three solutions of ozone in liquid oxygen were the most concentrated directly obtainable with the ozonizer employed. Extrapolation of their values of P_2 gives $P_\infty = 31$, but they are so close together that, in view of the small moment of the molecule, their differences from one another and from the true value of P_∞ are probably within the experimental error. The value 26 is, therefore, taken as being within two units of the correct value. If 31 is used instead of 26, the moment comes out higher by only 0.07. The temperature at which these measurements were made was so low as to raise a question of the necessity of applying the usually negligible quantum theory correction to the polarization. However, the probable moments of inertia of the molecule proved to be so large as to render the correction negligible. The molar refraction 7.6 calculated for gaseous ozone at 0° and 760 mm. seems a little high as compared to the value 4.05 calculated for gaseous oxygen under similar conditions from the refractive index in Landolt-Börnstein, but, even if the value were as low as 6.0 instead of 7.6, the moment would be raised only to 0.51. It is interesting to note that the polarization 3.86 found for liquid oxygen, which agrees closely with the values found by Kanda,⁶ is lower than the value 4.01 calculated for MR_D from the refractive in-

(4) Eisenlohr, "Spektrochemie organischer Verbindungen," F. Enke, Stuttgart, 1912.

(5) Miller, *THIS JOURNAL*, **56**, 2360 (1934).

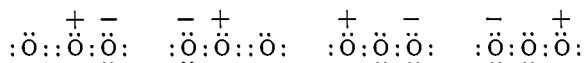
(6) Kanda, *J. Chem. Soc. Japan*, **12**, 473 (1937).

dex and density of liquid oxygen given by Landolt-Börnstein. The value of MR_D calculated for the gas at 0° and 760 mm. from data in Landolt-Börnstein is 4.05, and the refraction extrapolated to infinite wave length by means of a dispersion formula is 3.96. The same dispersion in the liquid would give $MR_\infty = 3.92$, which differs from the polarization 3.86 by no more than the uncertainty arising from the experimental errors in both figures. It is evident that not only is the dipole moment of the oxygen molecule zero but also the atomic polarization $P_A = P - MR_\infty$ is so small as to differ from zero by less than the experimental error. A very small atomic polarization is characteristic of small molecules.

The small but finite moment found for the ozone molecule shows that the symmetrical triangular structure , in which each oxygen is linked by a single bond to the two other atoms in the molecule, is impossible as this structure would have zero moment. It also shows the impossibility of a linear molecule in which a central oxygen is joined by identical bonds to one on each side of it. The infrared spectrum⁷ has been interpreted as indicating a triangular molecule, the angles of the triangle varying somewhat with the interpretation. The best results seem, however, to point to a molecule in which two atoms are bound to a central atom with an obtuse angle between the two bonds. Benedict⁸ even went so far as to calculate the angle as 122° and the bond distance as 1.29 Å. This bond distance value is close to that for the single oxygen-oxygen bond⁹ 1.32 Å., while the distance should probably be close to and slightly less than the double bond distance 1.14 Å. This cannot, therefore, be regarded as a satisfactory determination of the bond angle.

The natural expectation that the structure of ozone should be more or less analogous to that of sulfur dioxide is strengthened by the spectroscopic investigations. Electron diffraction¹⁰ shows the sulfur dioxide molecule to be a triangle with the O-S-O angle $124 \pm 15^\circ$ and the sulfur-oxygen separation 0.05 Å. less than the sum of the covalent radii for a double bond. A larger O-O-O angle might be expected in the ozone molecule because of the smaller size of the central atom. The electronic structures which seem likely to

contribute to the ground state of the molecule are the following



The first two structures, in which each atom has its complete octet of electrons, should make the largest contribution. All these structures are bent, the O-O-O angle being not less than 120° . The dipole moment should arise wholly from the first two structures and should be in the line bisecting the O-O-O angle, as the components of all the moments perpendicular to this line should cancel out. The moment of the molecule is the resultant of two equal moments in the two O-O bonds, that is, $2m \cos(\theta/2) = 0.49$, where θ is the O-O-O angle. If $\theta = 120^\circ$, $m = 0.49$, and, if $\theta = 170^\circ$, $m = 3$, which is about the size of the ordinary semi-polar bond between atoms of different elements¹¹ and identical with that between sulfur and oxygen.

The nitrogen-oxygen bond in the nitro group, which consists of equal contributions from a double bond form and from a single semi-polar bond form has a moment 3.3. On the other hand the molecule of nitrogen dioxide has been found to have a small moment like that of ozone, Williams, Schwingel and Winning¹² reporting a value 0.51 at 23.4° , which decreased with rising temperature, and Schultz¹³ finding a constant value 0.29. The nitrogen dioxide molecule, although it possesses one less electron, presumably has a triangular structure somewhat similar to that of ozone and, like ozone, the resultant of contributions from different forms. The resultant of the moment of these bonds would be in the line bisecting the O-N-O angle. The small difference in electronegativity between nitrogen and oxygen seems to have little effect upon the moment. The identity of the two bonded atoms might be expected to reduce the polarity of a semi-polar bond between them as compared to that of a bond between two atoms of different electronegativities, but the effect of electronegativity difference between the elements upon the moment of a semi-polar bond between them has thus far been obscured by the uncertainties of the bond moments. The dipole moment does not prove that the O-O-O angle is wider than 120° , but places the probable limits at 120 and

(7) Stuart, "Molekülstruktur," Verlag von Julius Springer, Berlin, 1934, p. 314.

(8) Benedict, *Phys. Rev.*, **43**, 580 (1933).

(9) Pauling, *Proc. Natl. Acad. Sci.*, **18**, 293 (1932).

(10) Cross and Brockway, *J. Chem. Phys.*, **3**, 821 (1935).

(11) Smyth, *This Journal*, **60**, 183 (1938).

(12) Williams, Schwingel and Winning, *ibid.*, **58**, 197 (1936).

(13) Schultz, *Z. Physik*, **109**, 517 (1938).

160°. It thus may be concluded that the ozone molecule is a triangular structure consisting of contributions from different forms. The two oxygens linked to the central atom form an angle of, perhaps, 140°. The two oxygen-oxygen bonds would then be expected to have lengths of about 1.13 Å. and moments not far from 0.7.

The low moment found for silicobromoform, SiHBr_3 , is consistent with the low values for the chlorosilanes found by Brockway and Coop in the vapor state¹⁴ and published after our measurements had been carried out. The value of SiHBr_3 , 0.79, is lower than the moment of SiHCl_3 , 0.85, just as that of CHBr_3 ,¹⁵ 0.99, is lower than that of CHCl_3 , 1.05, but the exact differences are uncertain because of solvent effect. Brockway and Coop have pointed out that the reduction of moment in the di- and trichlorosilane molecules because of mutual induction between the dipoles is less than in the corresponding carbon compounds because the larger size of the silicon separates the dipoles more. Although the moment of silicobromoform is smaller than that of bromoform, the difference is relatively smaller than that between methyl chloride and monochlorosilane. This same dependence of induction upon the size of the central atom has been observed² recently in the cases of mono and dichloro compounds of carbon, silicon, germanium and tin in extension of relations previously noted.¹¹

The moment of dichlorogermane, 2.20, is larger than that of methylene dichloride, 1.56, and much larger than that of dichlorosilane, 1.17, but much smaller than the moment of $(\text{C}_2\text{H}_5)_2\text{SnCl}_2$, 3.85, which should be close to the tin analog of these other compounds. If Müller's empirical equation for solvent effect¹⁶ applies to GeH_2Cl_2 as it does to CH_2Cl_2 , a gas value 2.34 may be calculated for GeH_2Cl_2 , which, for our present considerations, is not a material alteration from the solution value. The increase in moment with increase in the size and positive character of the central atom when the individual dipoles have their positive ends toward the latter has

been observed before.^{11,17} The sharp decrease from the carbon to the silicon compound in the cases of CH_2Cl_2 and SiH_2Cl_2 and CHBr_3 and SiHBr_3 as well as in the other chlorosilanes must arise in part, at least, from a resonance which involves contributions from forms containing positive halogen linked by a double bond to the central atom. This involves a shortening of the silicon-halogen bond below the sum of the single covalent bond radii of the two atoms, which amounts to 7.0% in SiHCl_3 and 7.4% in SiCl_4 , as compared to 0% in CCl_4 , 5.9% in GeCl_4 , and 3.8% in SnCl_4 . The percentage lowerings are calculated from the bond radii given by Pauling⁹ and the interatomic distances summarized by Brockway.^{14,18} They indicate clearly that the contribution of the doubly-bonded form, which, through having a positive charge on the halogen, lowers the total dipole moment of the molecule, is greatest in the silicon compounds. This would tend to make the moments of the silicon compounds have minimum values, but the difference between the bond shortenings in the two tetrachlorides appears too small to account wholly for the large difference in moment between the silicon and the germanium compounds. Undoubtedly, the more electropositive character of the germanium contributes largely to the difference.

Summary

The dipole moment of ozone has been measured in solution in liquid oxygen. It indicates that the molecule is a bent structure with a very obtuse angle between the bonds of two oxygens attached to a central atom. These two identical bonds have some polar character as a result of resonance among forms containing semi-polar bonds.

The moments of silicobromoform and dichlorogermane, measured in heptane and carbon tetrachloride solutions, respectively, show that silicon compounds tend to have minimum moments in the group of carbon, silicon, germanium and tin compounds, which, otherwise, increase in the order named.

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(14) Brockway and Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938).

(15) Smyth and Rogers, *THIS JOURNAL*, **52**, 2227 (1930).

(16) Müller, *Physik. Z.*, **34**, 689 (1933).

(17) Smyth, *J. Phys. Chem.*, **41**, 209 (1937).

(18) Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).