THE ANGLE BETWEEN THE OXYGEN BONDS BY THE COLLISION AREA METHOD

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The recent interesting predictions of Pauling[2] and Slater,[3] based on the quantum mechanics, regarding the angle between the valence bonds of the oxygen atom suggest the possibility and desirability of experimental test. Pauling states that the bond angle for the water molecule lies between the limits of 90 and $109^1/_2°$, closer to the former; while Slater believes it to be somewhat less than a right angle, assuming that the interaction of the two hydrogens would, by residual valence, decrease the normal angle. Both agree that except for the interaction of the two hydrogen atoms the bond angle would be about 90°, which is predicted to be the normal orientation of bonds formed by p-electrons.

The experimental evidence as to the angle of the oxygen bonds includes the following. (1) It has been shown by x-ray crystal structure studies that the angle between oxygen bonds in certain inorganic oxides, namely, Sb_4O_6 and As_4O_6, differs from the tetrahedral angle[4] by no more than 5°. (2) A simple potential energy study of the structure of the water molecule has been given by Debye,[5] who shows, assuming the water molecule to be made up of ions, that the only structure possible is that in which the ions are arranged in the form of an isosceles triangle; and by making use of the known values for the moments of inertia, he shows that the angle between the bonds must be approximately either 110 or 64°. Debye then proceeds to choose the smaller angle as more probable by a study of the dipole moment of the water molecule; but the choice is not very definite and we may consider either angle as possible. (3) The finite dipole moments of the ethers[6] indicate an angle of the oxygen bonds considerably less than 180°. (4) The ease of formation of the ozonides by bridging across double bonds and the entrance of oxygen into ring structures, as in the case of furan (which is nearly as stable as benzene), show that the oxygen bond angle is comparable with that between carbon bonds.

Our previous experience[7] with a method for matching molecule collision

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[1] Du Pont Fellow at The Ohio State University, 1931–32.

[2] Pauling, *Proc. Nat. Acad. Sci.*, **14**, 359 (1928); THIS JOURNAL, **53**, 1367 (1931).

[3] Slater, *Phys. Rev.*, **37**, 481 (1931).

[4] Ewald and Hermann, "Strukturbericht."

[5] Debye, "Polar Molecules," The Chemical Catalog Co., New York, 1929, p. 68.

[6] Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., New York, 1931, p. 87.

[7] (a) Melaven and Mack, THIS JOURNAL, **54**, 888 (1932); (b) Sperry and Mack, *ibid.*, **54**, 909 (1932).

areas, determined from gaseous viscosity, with average cross-sectional areas of models made to scale, suggested that it would be of interest to apply this method to an examination of the spatial configuration of the two phenyl groups in diphenyl ether, in an effort to arrive at a conclusion regarding the angle between the oxygen bonds which hold the phenyl groups.

Experimental

The sample of diphenyl ether, purchased from the Eastman Kodak Co., was fractionally distilled, washed with a concd. aqueous solution of sodium hydroxide, then several times with water, and finally dried over anhydrous calcium chloride. After repeated recrystallization from ethyl alcohol and from its own melt, it was twice fractionated in an efficient still-head and a portion having a boiling point of 257.3° (corrected at 746 mm.), and a melting point of 26.8–27.0°, was taken for use.

The viscosity of the vapor was measured over a temperature range of 176–363° by transpiration through a capillary in essentially the same manner already described. The only present differences in experimental technique involved the use of carefully constructed and controlled air-baths instead of water and oil thermostats, and the use of two sensitive quartz clicker-membranes instead of mercury manometers for measuring the influx and efflux pressures (p_1 and p_2). The latter change in apparatus was necessary because the volatilization temperature (150°) needed to produce the desired driving pressure would have developed a large enough pressure of mercury vapor, had mercury manometers been used, to interfere seriously with the rates of transpiration of the diphenyl ether vapor.

The usual precautions were taken to prevent turbulent flow; the viscosities η at the several temperatures were calculated[8] with Meyer's transpiration formula, as before,[7a] and were corrected for slip, η_c. Then the Sutherland constant, C, was computed graphically and the collision areas calculated by means of Chapman's equation.

TABLE I

VISCOSITY DATA AND COLLISION AREA FOR DIPHENYL ETHER

Temp., °C.	Influx press., p_2, cm.	Efflux press., p_2, cm.	Rate of flow, cc./hr.	η	η_c	C	Collision area, sq. Å.
176.0	2.272	0.13	0.5334[a]	0.8250×10^{-4}	0.8397×10^{-4}		36.32
199.1	2.335	.13	.5016	.8776	.8942		35.84
255.2	2.475	.17	.4550	.9680	.9956	400	36.10
330.8	2.550	.18	.3780	1.086	1.112		36.20
363.2	2.860	.19	.4302	1.138	1.165		36.20

Av. 36.13

[a] The density of liquid diphenyl ether at 150°, the temperature at which volatilization occurred, was determined to be 0.9650.

Before a model of diphenyl ether was made, the viscosity of the vapor of diphenylmethane, as a check on the results, was measured over a similar temperature range, and its collision area calculated in the same way.

[8] The present capillary (Pyrex) had a length of 27.53 cm., and an average radius of 0.02510 cm. (measured with a mercury thread). Calibration with dry air gave the following results for the viscosity of air: at 63°, 199×10^{-6}; at 103°, 216×10^{-6}; at 168°, 247×10^{-6}; at 212.5°, 262×10^{-6}; at 232°, 272×10^{-6}.

TABLE II

VISCOSITY DATA AND COLLISION AREA FOR DIPHENYLMETHANE

Temp., °C.	Influx press., p_1, cm.	Efflux press., p_2, cm.	Rate of flow, cc./hr.	η	η_c	C	Collision area, sq. Å.
165.8	2.008	0.125	0.4909[a]	0.8110×10^{-4}	0.8264×10^{-4}		36.44
218.5	2.160	.115	.4217	0.9026	0.9223	387	36.41
307.7	2.260	.180	.3358	1.049	1.076		36.36
360.7	2.320	.200	.2996	1.132	1.163		36.36

Av. 36.40

[a] The density of liquid diphenylmethane at 150°, the temperature at which volatilization occurred, was determined to be 0.9075. The melting point is 24.8°.

In the case of both substances, diphenyl ether and diphenylmethane, the plot of $T^{1/2}/\eta_c$ against T to get the Sutherland constant, C, gave points lying almost perfectly on a straight line. It will further be noted that the agreement between the two collision areas, 36.13 and 36.40 sq. Å., is gratifyingly close. This is as it should be, for the two molecules, both containing two phenyl groups and differing only to the extent that one contains an oxygen atom and the other a methylene group, should have substantially the same collision area. If we suppose that the two phenyl groups in *diphenylmethane* are attached to the carbon atom of the methylene group at a tetrahedral angle, as is probable, then it follows, quite apart from any model considerations, that the angle at which the two phenyl groups are attached to the oxygen atom in *diphenyl ether* is substantially tetrahedral.

Model Considerations.—A model of diphenyl ether was made up to scale, 1 inch = 1 Å., according to the principles of model construction already laid down.[9,7a] The benzene rings were flat hexagonal graphite rings, made of carbon atoms of diameter 1.42, with C–H internuclear distances of 1.02, and hydrogen atom gas kinetic domain radii of 0.72 (on the assumption that three hydrogen atoms per molecule partake in an average collision). A model of the ring dome domain (gas kinetic radius 2.0) was attached to each face of the benzene ring. The *aromatic* C–O internuclear distance was taken as 1.37, based on x-ray analysis,[10] and the oxygen domain radius as 1.20. This latter value was based on a consideration of the collision area of the water molecule, as well as on the collision area of carbon dioxide. Rankine[11] reports 1.17, and the radius of the oxygen ion is given by Wasastjerna as 1.32, which is doubtless a little too large for the domain radius of a chemically bound oxygen atom. As a matter of fact the size of the oxygen atom plays such an insignificant role in determining the total collision area of the molecule that any small error made in guessing its exact effective size can be neglected. The velocity of rotation about the spin

[9] Mack, THIS JOURNAL, 54, 2141 (1932).

[10] Huggins, *Phys. Rev.*, 28, 1094 (1926).

[11] Rankine, *Proc. Roy. Soc.* (London), A98, 369 (1921).

axes can readily be shown to be too slow to affect the collision area appreciably.

The shadow-graphic average cross-sectional area of the model at forty-two approximately equal-angle positions is given in Table III, where the various area values are listed for different angles between the oxygen bonds which hold the two phenyl groups.

TABLE III

SHADOW AREAS OF MODEL OF DIPHENYL

Angle of bonds	180°	150°	120°	90°	60°ᵃ	30°ᵃ
Shadow area	39.14	38.33	37.34	35.35	33.54	30.64

ᵃ The domes on the faces of the rings would not permit such small angles, unless the domes are fluid enough to bulge out on the opposite side of the ring. Such bulging is considered to be improbable.

While the shadow areas are not greatly different over this range of bond angles, they differ enough to allow a fairly clear-cut decision regarding the oxygen bond angles in diphenyl ether. The experimentally determined collision area of 36.13 sq. Å. (Table I) lies between the shadow areas corresponding to 120 and 90°. Even admitting a possible error of ±3% (and it could not be more than this even with a 10% error in the Sutherland constant) in the experimental collision area, the bond angle would have maximum and minimum values of about 130 and 85°. Interpolation of the actual experimental collision area of 36.13 sq. Å. yields 107°. Thus the angle between the oxygen bonds is found to be approximately tetrahedral in the diphenyl ether molecule.

Methyl Ether.—The viscosity data have been determined for methyl ether and the collision area (12.13 sq. Å.) calculated by Titani.[12] We have made a model of the molecule, using spinning methyl groups with a hydrogen domain radius of 0.49 as in the case of methane and ethane,[7a] and oxygen atom dimensions the same as in diphenyl ether, above. The value of the oxygen bond angle was varied from 180 to 90° (until the methyl groups slightly overlapped), and the following values were obtained for the model average cross-sectional areas (Table IV).

TABLE IV

SHADOW AREAS OF THE MODEL FOR METHYL ETHER

Bond angle	180°	150°	120°	90°
Shadow area	12.28	12.85	12.33	11.74

It will be observed that Titani's experimental value of 12.13 sq. Å. checks well with these listed values. Whether or not his value can be used to obtain a definite conclusion regarding the oxygen bond angle depends, of course, on the reliability of his data. It is most interesting to note,

[12] Titani, *Bull. Chem. Soc. Japan*, **4**, 277 (1929); **5**, 98 (1930).

however, that interpolation of his value between 12.33 at 120° and 11.74 at 90°, yields an oxygen bond angle of 110°, approximately tetrahedral.

Ethyl Ether.—Values for the viscosity of ethyl ether vapor are reported[13] over a considerable temperature range. Using these data we have calculated the Sutherland constant and the molecule collision area. The data and the results of the calculations are given in Table V.

TABLE V

VISCOSITY DATA AND COLLISION AREA FOR ETHYL ETHER

Temp., °C.	η	Sutherland constant	Collision area, sq. Å.
0.2	0.689×10^{-4}		18.14
7.4	.712		...
27.6	.771	380	...
100.2	.942		...
212.7	1.234		18.18

Since the molecule of ethyl ether is made up of two-link carbon chains which may coil up in various positions, it is impossible to draw a definite conclusion about the oxygen bond angle in this case. It is interesting, however, to assume a bond angle of about 110° and then to observe from model study the tightness of the average coiling in the gaseous state. The model of ethyl ether was therefore built, with a value of 0.63 for the hydrogen domain radius, on the assumption that two hydrogen atoms per molecule partake in an average collision. Three different structures were studied: (1) a molecule extended as nearly as possible in a straight line; (2) a molecule coiled as tightly as the end methyl groups (assumed to be spinning) would allow; (3) a molecule with static methyl groups, which allowed tighter coiling than in (2). The values obtained for the average shadow area of the different structures were

(1) Ethyl ether (extended)......................... 21.29
(2) Ethyl ether (tightly coiled, spinning CH_3)......... 19.14
(3) Ethyl ether (tightly coiled, non-spinning CH_3)...... 17.40

     Collision area from viscosity data............... 18.16

It will be observed that the molecule must be tightly coiled in the gaseous state, since the cross-sectional area of the extended model is much too large, even when neglecting the effects of spin around the longitudinal axis (small moment of inertia). This tightly coiled configuration agrees well with the tight coiling found for heptane (which one would predict also for pentane and hexane). In fact it is impossible to coil the molecule sufficiently to obtain a small enough collision area to fit the experimentally determined value, without assuming some inter-meshing of the end methyl groups, either spinning or non-spinning, perhaps in a cog-wheel manner.

[13] Landolt–Börnstein, "Tabellen," 1923, Vol. I, p. 171.

In concluding these remarks about the ether molecules it may be said that we were also interested in di-tertiary butyl ether. A search of the standard references indicated that the substance had never been prepared. A study of the model of this molecule makes it clear that it would be impossible to place two tertiary butyl groups on an oxygen atom at an oxygen bond angle as small as 110°. Hence it is probably difficult, if not impossible, to prepare this compound; or if formed at all it would probably be quite unstable. An attempt to prepare it by several standard methods of synthesis failed.

The nearly identical values of Sutherland's constant for diphenyl ether and diphenylmethane indicate that the attractive forces between the molecules in the gaseous state are nearly the same in the two cases, suggesting that the phenyl groups contribute all but an inappreciable fraction of the van der Waals forces of attraction in the vapor. It is rather surprising to note, however, that in the liquid state the two compounds have quite different molecular volumes. Thus at 150°, which should be a corresponding temperature since the boiling points are nearly the same, the densities differ by nearly 7%, the values being 0.9650 for the ether and 0.9075 for diphenylmethane. This relative decrease in the size of the molecular volume of the ether may plausibly be attributed to an increase in internal pressure arising from the presence of the oxygen atom, and due either to its strongly polar nature, or to a resulting orientation effect which permits a closer packing.

Summary

An application of the shadow-graphic collision area method has been made in a study of the oxygen bond angle.

The collision areas of diphenyl ether and diphenylmethane, which should be approximately the same, are shown to be 36.13 and 36.40 sq. Å., respectively, and the oxygen bond angle in diphenyl ether is shown to be approximately tetrahedral. In methyl ether the bond angle is also probably closely tetrahedral.

The ethyl ether molecule is found to be tightly coiled; a prediction is made regarding the impossibility of preparing synthetically di-tertiary butyl ether; and some remarks are made about the molecular volume of liquid diphenyl ether.

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