ELECTRIC MOMENT AND MOLECULAR STRUCTURE. IX. THE OXYGEN AND SULFUR VALENCE ANGLES

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A previous paper[1] has described the determination of the carbon valence angle in benzyl derivatives as the angle between two component dipole moments, the resultant of which is the moment of the molecule as a whole. Since the dipoles are so far removed from one another by interposition of the benzene ring that they apparently do not affect one another's moments appreciably, a very satisfactory result was obtained. The present paper attempts to determine the oxygen and sulfur valence angles by application of the same method to ethers and sulfides, although the treatment is complicated by the considerable moments between the carbons and the oxygen or sulfur atoms. At the same time it appears desirable to consider the moments of certain newly determined heterocyclic compounds together with those of closely related compounds in the literature.

Preparation of Materials

Benzene and heptane were prepared as previously described.[1] The other materials, except as noted, were obtained from the Eastman Kodak Company. The densities and refractive indices determined for the liquids are given as criteria of purity.

p-Bromoanisole.—Material (m. p. 12–13°) was dried with anhydrous calcium chloride and twice fractionally distilled under reduced pressure; b. p. 101.9–102.1° (18 mm.); n_D^{20} 1.56422; n_D^{25} 1.56212; d_4^{25} 1.4902; d_4^{50} 1.4597.

p-Bromophenetole.—Material (m. p. 2–4°) was dried with anhydrous calcium chloride and twice fractionally distilled under reduced pressure; b. p. 109.2–109.5° (17 mm.); n_D^{20} 1.55168; n_D^{25} 1.54950; d_4^{25} 1.4071; d_4^{50} 1.3768.

p-Bromodiphenyl Ether.—Material (b. p. 167–168° (15 mm.)) was dried with anhydrous sodium sulfate and fractionally distilled under reduced pressure; b. p. 171.6–171.7° (17 mm.); d_4^{25} 1.4155; d_4^{50} 1.3896.

4,4′-Dibromodiphenyl Ether.—Material (m. p. 57.5–58.5°) was twice fractionally crystallized from petroleum ether and dried in a vacuum desiccator; m. p. 58.8–58.9°.

4,4′-Dinitrodiphenyl Ether.—Material which had been recrystallized from alcohol, partially decolorized with norit, and finally crystallized from benzene, and had a m. p. 142–143°, was further purified by repeated treatments with "Darco" in benzene solution. After being twice fractionally crystallized from benzene and dried in an evacuated desiccator, it had only a very faint yellowish tinge, which could not be removed by further treatment with decolorizing materials; m. p. 144.4–144.7°.

4,4′-Dibromodiphenyl Sulfide.—Material, prepared by Mr. P. D. Hammond and kindly loaned for our measurements, had been purified by crystallization from glacial acetic acid and drying in a vacuum desiccator to remove acetic acid; m. p. 112.2–112.4°. This material was twice fractionally crystallized from a mixture of benzene and petroleum ether, washed with petroleum ether, and dried in a vacuum desiccator; m. p. 112.6–112.8°.

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[1] Smyth and Walls, THIS JOURNAL, 54, 1854 (1932).

Divinyl Ether.—Material[2] loaned by Dr. W. L. Ruigh of the Laboratory for Pure Research of Merck and Company, Inc., was dried over sodium wire and fractionally distilled; b. p. 28.31 ± 0.03° (758.7 mm.); n_D^{20} 1.39892.

Furan.—Material obtained from the Miner Laboratories, Chicago, was purified by fractional distillation through a soda lime tower as described in "Organic Syntheses," Vol. VII, p. 40 (New York, John Wiley and Sons, Inc., 1927); b. p. 31.3° (757 mm.); n_D^{20} 1.42150; n_D^{25} 1.41852; d_4^{20} 0.9378; d_4^{25} 0.9313.

Tetrahydrofuran.—This was prepared under the direction of Dr. Wallace H. Carothers of E. I. du Pont de Nemours and Company by catalytic reduction of the above described furan in butyl alcohol solution. It was purified by fractional distillation through a 1.8-meter fractionating column, dried with anhydrous sodium sulfate, decanted and fractionally distilled; b. p. 64.0–64.1° (755 mm.); n_D^{20} 1.40550; n_D^{25} 1.40355; d_4^{20} 0.8966; d_4^{25} 0.8910; d_4^{50} 0.8631.

Experimental Results

The densities and dielectric constants of the solutions of the polar substances in the non-polar were measured with the apparatus and methods previously employed,[1,3] a wave length of 1000 meters being used in the dielectric constant determinations.   In Table I the first column gives the

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

c_2	ϵ 25°	50°	d 25°	50°	P_2 25°	50°
			Benzene–p-Bromoanisole			
0.00000	2.276	2.226	0.8734	0.8465	(26.68	26.76 = P_1)
.01723	2.402	2.338	.8882	.8610	141.6	135.3
.02893	2.488	2.416	.8984	.8712	140.4	135.0
.04318	2.591	2.508	.9105	.8833	138.3	132.9
.06374	2.738	2.639	.9273	.9003	135.6	130.2
.06900	2.776	2.672	.9317	.9046	135.0	129.6
.09091	2.929	2.809	.9493	.9225	132.1	127.0
			Heptane–p-Bromoanisole			
0.00000	1.920	1.883	0.6795	0.6577	(34.58	34.62 = P_1)
.02183	2.013	1.967	.6950	.6730	148.2	141.8
.04528	2.114	2.058	.7115	.6893	145.7	139.3
.06302	2.191	2.128	.7239	.7017	143.8	137.7
.07361	2.238	2.169	.7317	.7091	142.6	136.5
.10479	2.375	2.293	.7542	.7313	139.0	133.6
.14445	2.549	2.452	.7831	.7597	134.4	130.1
			Benzene–p-Bromophenetole			
0.00000	2.278	2.228	0.8734	0.8465	(26.70	26.78 = P_1)
.01124	2.371	2.311	.8830	.8557	161.9	155.8
.02059	2.449	2.381	.8910	.8638	160.3	154.5
03451	2.565	2.483	.9023	.8751	158.2	152.3
.05200	2.706	2.611	.9167	.8893	155.4	149.7
.07009	2.850	2.738	.9310	.9035	152.4	146.8
.09847	3.072	2.936	.9531	.9254	148.0	142.9

[2] Ruigh and Major, THIS JOURNAL, **53**, 2662 (1931).

[3] Smyth and Walls, *ibid.*, **53**, 527 (1931).

TABLE I (*Continued*)

c_2	ϵ		d		P_2	
	25°	50°	25°	50°	25°	50°
Heptane–*p*-Bromophenetole						
0.00000	1.920	1.883	0.6795	0.6577	(34.58	34.62 = P_1)
.02289	2.030	1.983	.6958	.6740	167.8	160.9
.03849	2.105	2.051	.7068	.6849	165.3	158.8
.06489	2.233	2.168	.7259	.7036	161.3	155.7
.10200	2.413	2.331	.7524	.7297	156.3	151.1
.13172	2.558	2.464	.7738	.7509	152.4	147.8
Benzene–*p*-Bromodiphenyl Ether						
0.00000	2.276	2.226	0.8734	0.8465	(26.68	26.76 = P_1)
.01589	2.342	2.286	.8905	.8636	111.7	108.6
.03227	2.408	2.349	.9080	.8810	111.0	109.2
.04916	2.476	2.410	.9251	.8981	110.9	108.5
.07661	2.581	2.507	.9515	.9246	110.0	107.7
.10200	2.674	2.597	.9750	.9480	109.0	107.5
Heptane–*p*-Bromodiphenyl Ether						
0.00000	1.920	1.883	0.6795	0.6577	(34.58	34.62 = P_1)
.01919	1.972	1.931	.6969	.6750	116.9	113.8
.04042	2.030	1.986	.7158	.6938	116.7	114.5
.07109	2.114	2.063	.7431	.7209	115.6	112.8
.11641	2.240	2.178	.7825	.7600	113.9	110.9
Benzene–4,4′-Dibromodiphenyl Ether						
0.01144	2.293	2.242	0.8942	0.8669	76.5	76.6
.01656	2.299	2.248	.9031	.8758	76.2	75.7
.02482	2.310	2.260	.9177	.8903	75.8	76.3
.03307	2.321	2.271	.9316	.9040	76.3	76.7
.04389	2.335	2.284	.9498	.9221	76.4	76.2
.06571	2.362	2.313	.9848	.9571	76.4	76.8
Heptane–4,4′-Dibromodiphenyl Ether						
0.01555	1.939	1.902	0.7018	0.6801	75.1	74.5
.02773	1.952	1.914	.7174	.6954	76.4	75.5
.03367	1.960	1.922	.7253	.7033	77.7	76.5
.04351	1.972	1.934	.7388	.7165	77.6	76.9
.04543	1.974	1.936	.7415	.7193	77.3	76.4
Benzene–4,4′-Dinitrodiphenyl Ether						
0.00000	2.2755	2.2255	0.8733	0.8464	(26.66	26.74 = P_1)
.00202	2.299	2.246	.8757	.8488	224.7	209.9
.00308	2.311	2.257	.8770	.8500	221.5	211.8
.00343	2.315	2.260	.8773	.8503	222.0	210.4
.00473	2.330	2.274	.8788	.8518	221.2	210.6
.00482	2.330	2.274	.8789	.8519	217.6	209.3
.00596	2.342	2.286	.8803	.8533	214.6	209.6
.00690	2.352	2.295	.8812	.8542	213.1	207.9
.00983	2.381	2.322	.8846	.8575	210.8	203.7

TABLE I *(Concluded)*

c_2	ϵ		d		P_2	
	25°	50°	25°	50°	25°	50°
Benzene–4,4′-Dibromodiphenyl Sulfide						
0.00000	2.2755	2.2255	0.8733	0.8464	(26.66	26.74 $= P_1$)
.00833	2.290	2.240	.8891	.8620	85.5	85.6
.00839	2.290	2.240	.8893	.8623	85.1	85.1
.01240	2.297	2.247	.8967	.8696	84.7	85.6
.01724	2.305	2.255	.9055	.8785	84.7	84.7
.02169	2.314	2.263	.9137	.8866	85.7	85.3
.02556	2.319	2.269	.9207	.8935	84.6	85.0
.02979	2.326	2.276	.9283	.9011	84.7	84.8
.03075	2.329	2.278	.9300	.9027	85.2	85.3
.03692	2.335	2.285	.9410	.9138	86.0	86.1
.04079	2.345	2.295	.9477	.9205	85.0	85.1
Benzene–Furan						
0.0000	2.276		0.08734		(26.68	$= P_1$)
.0286	2.289		.8748		28.4	
.0608	2.306		.8763		28.8	
.0664	2.308		.8765		28.8	
.1338	2.340		.8796		28.6	
.1355	2.341		.8797		28.6	
.1731	2.363		.8816		28.8	
1.0000	2.953		.9313		28.8	
Benzene–Tetrahydrofuran						
0.00870	2.314	2.258	0.8737	0.8467	85.3	79.6
.00888	2.315	2.259	.8737	.8468	86.4	79.7
.01040	2.322	2.266	.8737	.8468	86.3	81.6
01770	2.357	2.296	.8739	.8471	88.8	83.3
.01887	2.365	2.303	.8739	.8472	90.8	85.0
1,4-Dioxane–Tetrahydrofuran						
0.00000	2.261	2.214	1.0312	1.0027	(25.27	25.30 $= P_1$)
.01778	2.347	2.291	1.0314	1.0028	87.2	83.7
.01898	2.352	2.296	1.0313	1.0027	87.0	83.3
.03259	2.419	2.355	1.0295	1.0010	87.9	83.9
.05522	2.533	2.454	1.0264	0.9978	87.8	83.6
.07986	2.660	2.569	1.0230	0.9944	87.3	83.8
	20°		20°		20°	
Benzene–Divinyl Ether						
0.00000	2.286		0.8786		(26.65 $= P_1$)	
.04185	2.340		.8742		45.77	
.07059	2.380		.8712		46.06	
.09017	2.406		.8692		45.95	
.11617	2.443		.8666		46.02	
.14231	2.479		.8638		45.97	
.17611	2.527		.8602		45.96	
.22112	2.593		.8556		45.96	
1.00000	3.942		.7722		44.91	

mole fraction c_2 of the polar substance in the solution and the succeeding columns give the values at 25 and 50° of the dielectric constants ϵ, the densities d of the solutions and the polarizations P_2 of the polar substance. The values of the molar refraction MR_D and of the moment μ in Table II were obtained as in previous papers.[1]

TABLE II

REFRACTIONS, ORIENTATION POLARIZATIONS AND ELECTRIC MOMENTS

Compound	Solvent	MR_D	$P_\infty - MR_D$		$\mu \times 10^{18}$	
			25°	50°	25°	50°
p-Bromoanisole	Benzene	40.70	103.1	97.3	2.23	2.25
	Heptane		110.3	102.8	2.30	2.31
p-Bromophenetole	Benzene	45.47	118.1	111.8	2.38	2.41
	Heptane		125.7	117.9	2.46	2.48
p-Bromodiphenyl ether	Benzene		50.6	47.7	1.56	1.58
	Heptane	61.8[a]	56.4	53.5	1.65	1.67
4,4'-Dibromodiphenyl ether	Benzene	69.0[a]	7.4	7.5	0.60	0.62
	Heptane		8.1	7.4	0.62	0.62
4,4'-Dinitrodiphenyl ether	Benzene	65.5[a]	162.0	150.0	2.79	2.80
4,4'-Dibromodiphenyl sulfide	Benzene	76.5[a]	8.7	8.7	0.65	0.67
Divinyl ether	Benzene	21.94[b]	24.0[b]		1.06[b]	
Furan	Benzene	18.43	10.4		0.71	
Tetrahydrofuran	Benzene	19.76	60.9	56.2	1.71	1.71
	1,4-Dioxane		67.8	64.0	1.81	1.83

[a] Calculated from refractive indices and densities of solutions. [b] Measurements made at 20°.
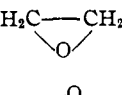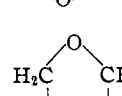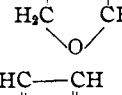
Discussion of Results
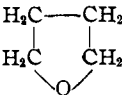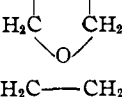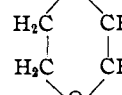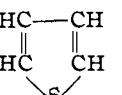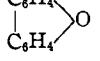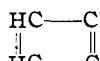
It is interesting to note in Table II that the moments found for p-bromoanisole, p-bromophenetole and p-bromodiphenyl ether in benzene solution are 0.07–0.09 × 10⁻¹⁸ lower than the values found in heptane solution, which is the reverse of the situation in the case of the ethylene halides treated in a previous paper.[4] The differences are so small, however, that the conclusions to be drawn are not materially affected by using only the values obtained in benzene, which was a better solvent for the larger molecules and which was generally used in the measurements taken from the literature. The low values for 4,4'-dibromodiphenyl ether and the corresponding sulfide may be, at least, 0.2 × 10⁻¹⁸ too high because of neglect of the atomic polarization in the calculation. The P_2-c_2 curve for tetrahydrofuran in benzene is very different from that in dioxane, but the value found for the moment in benzene is but slightly lower. Its use, rather than that of an average value, will not affect the conclusions to be drawn.

The values adopted for the moments and those taken from the literature[5] for use in calculation or discussion are listed in Table III.

[4] Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4242 (1931).

[5] See Smyth, "Dielectric Constant and Molecular Structure," New York, The Chemical Catalog Company. Inc.. 1931, Appendices I and II.

TABLE III
ELECTRIC MOMENTS ($\times 10^{18}$)

C_6H_5Cl	1.52	$C_6H_5OCH_3$	1.2	H_2C——CH_2		
C_6H_5Br	1.50	p-$ClC_6H_4OCH_3$	2.24			
$C_6H_5NO_2$	3.9	p-$BrC_6H_4OCH_3$	2.24	H_2C CH_2	1.71	
H_2O	1.85	p-$O_2NC_6H_4OCH_3$	4.36	O		
H_2S	0.95	$C_6H_5OC_2H_5$	1.0			
$(CH_3)_2O$	1.29	p-$BrC_6H_4OC_2H_5$	2.40	H_2C——CH_2		
$(C_2H_5)_2O$	1.12	C_6H_5OH	1.70	O		
$(CH_2=CH)_2O$	1.06	p-ClC_6H_4OH	2.68		1.88	
C_2H_5OH	1.70	p-BrC_6H_4OH	2.86	O		
C_2H_5SH	1.39[6]	p-$O_2NC_6H_4OH$	5.05	H_2C CH_2		
$(C_2H_5)_2S$	1.57[6]	C_6H_4				
$(C_6H_5)_2O$	1.05	C_6H_4⟩O		H_2C CH_2		
$(p$-$BrC_6H_4)_2O$	0.6		0.9	O	0.4	
$(p$-$O_2NC_6H_4)_2O$	2.80					
p-$BrC_6H_4OC_6H_5$	1.57					
$(C_6H_5)_2S$	1.47	HC——CH		HC——CH		
$(p$-$BrC_6H_4)_2S$	0.6	‖ ‖		‖ ‖	0.6	
p-$ClC_6H_4SC_6H_5$	1.76	HC CH	0.7	HC CH		
		O		S		

The method of calculating the oxygen valence angle θ is obvious from consideration of Fig. 1. The calculation is somewhat complicated by the presence of the dipoles in the directions of the C–O bonds and it is necessary to assume that these moments, as well as θ, are unaffected by the moments in the bonds of the para-substituted groups and *vice versa*. The validity of this assumption has been discussed in the previous paper dealing with the carbon valence angle, where it seems fully justified by the results. It may be a more inexact approximation in the case of the ethers and sulfides, where the C–O and C–S moments are immediately adjacent to the ring. Our ignorance of the absolute value of the small moment probably existing in the C–H bond causes no error in the calculati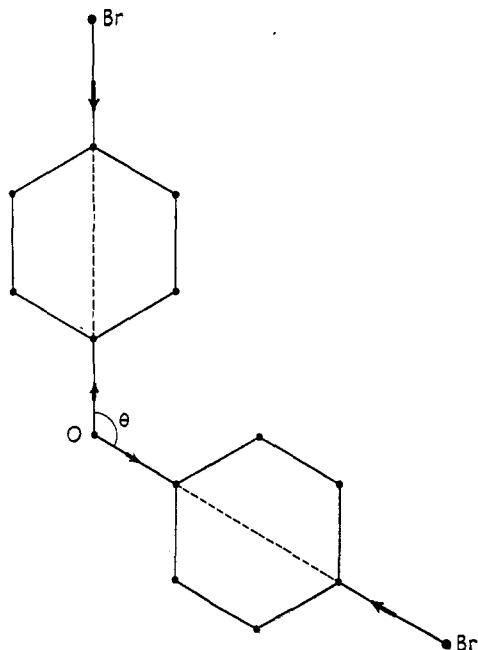ons since it cancels out when a set of simultaneous equations for the moments involved in the diphenyl ethers is solved. This is apparent in the following calculation given as an example.

Fig. 1.—The 4,4'-dibromodiphenyl ether molecule.

[6] Hunter and Partington, *J. Chem. Soc.*, 2062 (1931).

$$C_6H_5Br \quad m_{C-H} + m_{C-Br} = 1.50 \times 10^{-18} \tag{1}$$
$$(C_6H_5)_2O \quad 2(m_{C-H} + m_{C-O}) \cos \theta/2 = 1.05 \times 10^{-18} \tag{2}$$
$$(p\text{-}BrC_6H_4)_2O \quad 2(m_{C-Br} - m_{C-O}) \cos \theta/2 = 0.6 \times 10^{-18} \tag{3}$$

Adding (2) and (3) and substituting (1), we have

$$3.00 \cos \theta/2 = 1.65, \text{ whence } \theta = 113°$$

In the cases of the monosubstituted ether and sulfide, the equation for the resolution of two unequal vectors has, of course, to be used. The angles calculated for oxygen and sulfur in the diphenyl ethers and sulfides by this method are given in Table IV.

TABLE IV

VALENCE ANGLES OF OXYGEN AND SULFUR

$(p\text{-}BrC_6H_4)_2O$	113°	$(p\text{-}BrC_6H_4)_2S$	146°
$p\text{-}BrC_6H_4OC_6H_5$	124°	$p\text{-}ClC_6H_4SC_6H_5$	147°
$(p\text{-}O_2NC_6H_4)_2O$	121°		

The angle calculated for $p\text{-}BrC_6H_4OC_6H_5$ is obtained by using the values of $(m_{C-H} + m_{C-O})$ and $(m_{C-Br} - m_{C-O})$ given by equations (2) and 3). The difference between the values of the angle for the monobromo and the dibromo ether is without significance. If the moment of the latter is taken as 0.4×10^{-18}, which may be more nearly correct than 0.6×10^{-18}, the angles calculated rise to 123 and 129°. The mean of these four rough values happens to be 122°, in excellent agreement with the value for $(p\text{-}O_2NC_6H_4)_2O$, which, being calculated from a large moment, is much more accurate than the others. If the presence of the nitro group increased the C–O moment by 0.15×10^{-18}, the value of θ would be lowered by only 3°, while, if the nitro group moment were increased at the same time, the lowering of the value calculated for θ would be less.

When $(p\text{-}BrC_6H_4)_2S$ is treated like the ether, a value of 98° is obtained for the sulfur valence angle, but, in the monochloro compound, the impossible value of -2 is obtained for cos θ. It, therefore, becomes necessary to suppose that m_{C-S} is greater than m_{C-Br}, that is $(m_{C-Br} - m_{C-S})$ is negative. The large angles given in Table IV are then obtained, the negligible difference between the moment of C_6H_5Cl, and that of C_6H_5Br being disregarded. If the moment of $(p\text{-}BrC_6H_5)_2S$ is taken as 0.5×10^{-18} instead of 0.6×10^{-18}, the angles calculated are 142 and 140°. The value calculated by Bergmann, Engel and Sándor[7] from their determination for $p\text{-}ClC_6H_4SC_6H_5$, which is the one here used, is 142°. When the equations used in calculating are solved for $m_{C-H} + m_{C-S}$, the value 2.5×10^{-18} is obtained, which is surprisingly high in comparison with the approximate figure 1.1×10^{-18} for $m_{C-H} + m_{C-O}$. This high value is not, however, irreconcilable with the moments of other sulfur compounds. The moment of the hydrogen sulfide molecule is little more than half that of the water

7 Bergmann, Engel and Sándor, Z. physik. Chem., [B] 10, 397 (1930).

molecule, but replacement of hydrogen by an alkyl group in the sulfur compound raises the moment, while the moment is lowered by a similar change in the case of the oxygen compound. This is evident in the results of Hunter and Partington,[6] in Table III, which are in excellent agreement with values calculated by one of the writers.[8] If the value of the moment of p-$ClC_6H_4SC_6H_5$ obtained by Bergmann, Engel and Sándor is correct and if, as has been assumed, the moment of the para-substituted group is approximately independent of the other moments in the molecule, the large value of about 146° must be accepted for the sulfur valence angle in these diphenyl sulfides.

As methyl and ethyl ethers, anisole, phenetole and diphenyl ether have moments of the same magnitude, it is natural to suppose that the valence angles and the R–O moments in all these compounds are much the same whether R is an alkyl or a phenyl group. However, the moments of the para-halogenated anisoles and phenetoles are much higher than that of p-bromodiphenyl ether and it is impossible to calculate their moments on the basis of these assumptions. Actually, the alkyl halides have moments from 0.3–0.5×10^{-18} higher than the phenyl halides. If the R–O moment when R is an alkyl group is taken as 1.8×10^{-18} as compared to a value of 1.1×10^{-18} obtained for R–O from the phenyl ethers, oxygen valence angles lying between 130 and 140° are obtained for the anisoles, methyl ether and the hydroquinone ethers, the equation for rotating dipoles being used in these latter calculations, and still larger angles are obtained for the phenetoles and ethyl ether. A larger angle in the phenetoles gives a lower moment to the unsubstituted compound and a higher one to the substituted as observed. If the H–O moment in the phenols is taken as 2.4×10^{-18}, instead of 1.6×10^{-18} as used by Eucken and Meyer,[9] the oxygen valence angles in the unsubstituted and in the p-chloro- and p-bromophenols are calculated as having values from 127 to 141°, the angle in p-nitrophenol being 152°. This H–O value gives a valence angle of 134° for water and, combined with the R–O value, 1.8×10^{-18}, an oxygen angle of 136° in the alcohols, the mutual inductive effects being neglected in both cases.

The difference between the phenyl R–O moment and the value assigned to that of the alkyl R–O is greater than would be expected. The experimental data on the anisoles and phenetoles are satisfactory, as evidenced, for example, by the identity of the value for p-bromoanisole obtained in the present investigation with that for p-chloroanisole obtained by Bergmann, Engel and Sándor.[7] Impurities, which might be present in small quantities only, should tend to lower the apparent values of the moments and thus make the difference between these substances and the diphenyl

[8] Smyth, THIS JOURNAL, **46**, 2151 (1924).

[9] Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929).

ethers appear less. The necessary neglect of the atomic polarization tends to make all the values a little high, but should not affect their comparison with one another or seriously alter the values of the angles calculated. It is evident that the moments of the substituted phenols are practically useless as a means of calculating the oxygen valence angle, possibly because of a shift to a quinoid structure. An example of this is probably found in p-nitroaniline, which has a moment, 7.1×10^{-18},[10] larger than the sum of the nitro and the amino moments acting in the same direction. The transmission of a large inductive effect through the ring could account for these discrepancies in the molecules which have two unlike groups attached to the oxygen, perhaps causing the apparent difference between the phenyl and the alkyl R–O moments. The transmission of such large effects appears consistent with chemical behavior but difficult to reconcile with the mutual independence of simple dipoles in meta- and para-disubstituted benzenes as summarized in the treatment of the carbon valence angle.[1] If such transmission were to occur from the two like substituents in the p,p'-disubstituted diphenyl ether, the two transmitted effects would so cancel each other as greatly to reduce the error caused in the calculated valence angle. In view of the uncertainty as to the interpretation of the data for the anisoles and phenetoles, it may be concluded only that there is an indication of the possibility of an oxygen valence angle larger than that found in the diphenyl ethers. It is obvious that the values used for the H–O and alkyl R–O moments cannot be regarded as determinations of these quantities.

If, in diphenyl ether, the C–C nuclear separation in the ring is taken as 1.42 Å.,[11] the C–O distance as 1.43 Å. and the C–H distance as 1.06 Å.,[12] and the hydrogen nuclei are assumed to be surrounded by repulsive spheres of radius 1.20 Å., calculation shows that, if the two benzene rings lay in the same plane, the oxygen valence angle would be widened to 169°. Indeed, with the rings in the same plane and an oxygen angle of 114°, the protons in the ortho position would be coincident. As the most reliable determination of this angle in the diphenyl ethers gives approximately 121°, it appears probable that the two rings oscillate about positions of minimum potential energy in which their planes are perpendicular to that of the oxygen valence angle.

In diphenylene oxide, if the external valences of the benzene rings made 120° angles with the adjacent sides of the hexagon in the normal fashion, the five-membered ring would be so distended that the C–O–C distance would be 2.99 Å. even if the oxygen valence angle were widened to 180°.

[10] Höjendahl, *Physik. Z.*, **30**, 391 (1929).

[11] Lonsdale, *Proc. Roy. Soc.* (London), **123**, 494 (1929); Wierl, *Ann. Physik*, [5] **8**, 521 (1931).

[12] Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

As this is more than double the C–O distance of 1.43 Å., it is evident that the carbon valence angles in this ring must be reduced below 120°, while the oxygen angle must be widened probably to more than 130°. As the force required to stretch a bond is much greater than that required to bend it, tension in the ring should be reduced more by alteration of the angles than by change of the internuclear distances, although both presumably occur. An exact quantitative treatment of this and of similar moments is impossible because of our ignorance of the size of effects, such as the adjustment of angles to lessen the ring tension, the stretching of bonds, the effect of such stretching upon bond moments, the size of the C–H dipoles and the angles which they make with the other parts of the molecule, but it is evident that the moment is markedly lower than those of ethyl, vinyl and phenyl ethers, as would be expected from the widening of the oxygen angle. If the furan ring were regarded as containing two double bonds, the carbon valence angles in the ring should tend to be 125°,[13] which would mean an even greater widening of the oxygen valence angle than in diphenylene oxide, perhaps to more than 140°, and a correspondingly lower moment, as observed. Since, however, the molar refraction MR_D, found for furan is 0.7 lower than the value calculated for it on the assumption of the occurrence of two double bonds in the ring, this simple explanation of the low moment is highly speculative.

The angle in a regular pentagon is 108°, but, in tetrahydrofuran, the fact that the C–O distance is about 1.43 Å. and the C–C about 1.54 Å. necessitates an alteration of the angles. It is impossible to say precisely what the oxygen angle is, but geometrical considerations indicate that it is probably not far from 100°, which causes the moment to be much higher than in the unsubstituted oxides previously discussed. As tetrahydrofuran is radically different in properties from furan, it may be that the disappearance of unsaturation also contributes to the increase in moment. This would accord with the assignment of a higher moment to the alkyl R–O. If the interatomic distances remain unchanged in the triangular ethylene oxide molecule, the oxygen valence angle is 65°, and the carbon angles in the ring 57.5°, which necessitates a higher moment than that of tetrahydrofuran, as observed, although the difference is less than would be expected. The very small moment, indistinguishable from zero, of dioxane indicates that the structure conforms to a symmetrically distorted hexagonal model with the four carbons in a plane and one oxygen above and the other below. The very small moment of thiophene shows a structure analogous to that of furan with a large sulfur valence angle of possibly 140° or more.

The heterocyclic compounds which have been discussed show the wide variation which the oxygen valence angle may be forced to undergo, from

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[13] This angle would result if the double bond were formed by the sharing of an edge between two regular tetrahedra. *Cf.* Slater, *Phys. Rev.*, **37**, 481 (1931).

65° to, perhaps, 140°. Because of the fact that the effects upon one another of the different moments in the molecule may not be wholly negligible, as well as because of the experimental error, the oxygen valence angle in the diphenyl ethers cannot positively be taken as 121°. However, the previously advanced reasons for deciding these effects to be small are sufficient to warrant the conclusion that the angle is correct to within ±5°. It is evident that the 90° angle calculated by the wave mechanics[14] may be much altered by the groups with which the oxygen combines.

Summary

The electric moments of para-substituted diphenyl ethers and a sulfide, an anisole, a phenetole and heterocyclic compounds have been determined and used, together with other moments taken from the literature, to study the angles between the valences in the oxygen and sulfur atoms.

The oxygen valence angle in the diphenyl ethers is found to be 121 ± 5°. The results for the anisoles and phenetoles, which are more complex, do not give dependable values for the oxygen angle, although they may be explained in terms of an oxygen angle not far from 135°. Limited data give for the sulfur valence angle in the diphenyl sulfides a value of about 146°, which may be too high. The oxygen valence angles in various heterocyclic compounds calculated from the interatomic distances vary from 65 to about 140° and the moments are in excellent qualitative agreement with predictions based on the size of the angles. The behavior of thiophene is strictly analogous to that of the corresponding oxygen compound.

14 Slater, *Phys. Rev.*, **37**, 481 (1931); *ibid.*, **38**, 1109 (1931): Pauling, THIS JOURNAL, **53**, 1367 (1931).

PRINCETON, NEW JERSEY

THE ACTION OF HYDRIODIC ACID ON STANNIC OXIDE

BY EARLE R. CALEY

The recent note of Laubengayer and Brandt[1] on a method for the preparation of germanium tetraiodide by the action of hydriodic acid on germanium dioxide leads me to mention an analogous reaction that I first observed some months ago and to which I can find no reference in the chemical literature.

It is a well-known fact that stannic oxide, especially ignited stannic oxide, is very resistant toward the usual chemical reagents. It was found, however, that concentrated hydriodic acid acts readily on stannic oxide, converting the latter into stannic iodide. With constant boiling hydriodic acid the reaction commences at about 90–95° and takes place quite

1 Laubengayer and Brandt, THIS JOURNAL, **54**, 621 (1932).