prevent spattering, but after the sample had thoroughly charred and was no longer liquid, the flame was turned on full with plenty of air to accomplish oxidation.

Anal. Subs., 0.1306: Ag, 0.0237. Calcd. for $AgNO_3 \cdot 2(C_7H_7)_2S$: Ag, 18.28. Found: Ag, 18.15.

C. Other Attempts.—Besides the unsuccessful attempts to prepare addition compounds of benzyl sulfide and silver halides, referred to in the above, attempts were also made to prepare them directly from the silver halides and benzyl sulfide, in the presence of alcohol. The results were negative.

Each of the cadmium halides was also mixed with benzyl sulfide in varying proportions and dissolved in alcohol and in acetone, but in no instance was a new product obtained.

Summary

1. The following new addition compounds of cuprous halides and silver nitrate with benzyl sulfide have been prepared and described: $CuCl \cdot 2(C_7H_7)_2S$, $CuBr \cdot 2(C_7H_7)_2S$, $CuI \cdot 2(C_7H_7)_2S$ and $AgNO_3 \cdot 2(C_7H_7)_2S$.

2. The addition compounds of cuprous halides with benzyl sulfide in alcohol or acetone solution have been shown to be in equilibrium with benzyl sulfide and the cuprous halide as indicated by the equation

$$CuX \cdot 2(C_7H_7)_2S, \rightleftharpoons CuX + 2(C_7H_7)_2S$$

3. Similar attempts to prepare addition compounds of benzyl sulfide with silver halides and with cadmium halides met with failure.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. IX. THE ELECTRIC MOMENTS OF CERTAIN SUBSTITUTED PHENOLS AND THEIR RELATION TO THE STEREOCHEMISTRY OF THE OXYGEN ATOM

BY JOHN WARREN WILLIAMS AND JOHN M. FOGELBERG

RECEIVED NOVEMBER 14, 1929 PUBLISHED APRIL 7, 1930

Introduction

Studies of electric moment data are beginning to give considerable information concerning the structure of molecules. It has, for example, been quite definitely established that the four valences of the carbon atom are directed toward the corners of a regular tetrahedron.[1,2] The structures of the simple polar molecules, water and ammonia, as deduced from infra-red

---

[1] (a) Williams, *Physik. Z.*, **29**, 683 (1928); (b) *Z. physik. Chem.*, **138A**, 75 (1928); (c) *Chemical Reviews*, **6**, 589 (1929).

[2] Höjendahl, "Studies of Dipole Moment," Dissertation, Copenhagen, **1928**.

absorption spectra,[3] seem to be in agreement with the conclusions which have to be drawn from electric moment studies. These configurations have been at least partially substantiated in the case of the oxygen atom by electric moment data of one of us,[1,4] and appear to be substantiated in the case of the nitrogen atom by the electric moment data for the substitution products of ammonia which have been calculated by Höjendahl[2] from dielectric constant data of Pohrt.[5] However, it is only fair to say that these latter data must be used with caution, since they are, in every case where a comparison is possible, only in approximate agreement with the results of the more recent measurements undertaken solely for the purpose of the calculation of the electric moment. In addition, one would have to conclude from them that the polarity of a molecule was dependent on the length of the hydrocarbon chain, although the contrary has been proved in the case of the alcohols[6] and ketones.[7] It is the purpose of this article to present electric moment data for a number of substituted phenols and to discuss their significance, particularly from the standpoint of the stereochemistry of the oxygen atom.

Experimental Data

The electric moments of the several molecules have been obtained by the method of the binary mixture, completely described in the previous papers of this series.[8] All dielectric constant and density determinations were made at 25°. All chemicals used were subjected to rigorous purifications. In short, every precaution for precision measurements was taken. The method of measurement of the dielectric constants was that now used by a number of investigators.[9] A frequency of 10^6 cycles was used.

The dielectric constant and density data for the various binary mixtures are presented in Table I. In this table f_1 is mole fraction of the solvent, benzene; d_4^{25} is density of the solution; ϵ is its dielectric constant; $P_{1,2}$ is molar polarization of the solution $= \left(\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_1M_1 + f_2M_2}{d} = f_1P_1 + f_2P_2\right)$ and P_2 is molar polarization of the solute molecule, that is, the molecule whose electric moment is being determined. The quantity $f_1M_1 + f_2M_2$ is a fictitious molecular weight of the solution, being made up of the mole

[3] Eucken, *Z. Elektrochem.*, **26**, 377 (1920); Heisenberg, *Z. Physik*, **26**, 196 (1924); Hund, *ibid.*, **31**, 81 (1925); **32**, 1 (1925); Debye, "Polar Molecules," Chemical Catalog Co., New York, **1929**, Chapter IV; Barker, *Phys. Rev.*, **33**, 684 (1929); Badger and Cartwright, *ibid.*, **33**, 692 (1929).

[4] Williams, *Physik. Z.*, **29**, 271 (1928).

[5] Pohrt, *Ann. Physik*, **42**, 569 (1913).

[6] Mahanti and Das Gupta, *Ind. J. Physics*, **3**, 467 (1929).

[7] Wolf and Lederle, *Physik. Z.*, **29**, 948 (1928).

[8] For a discussion of the method, and of the assumptions and approximations which must be made in its use, see Williams and Krchma, THIS JOURNAL, **49**, 1676 (1927).

[9] See Sack, *Ergebn. d. exakt. Naturwiss.*, VIII, 307 (1929).

fraction of the solvent times its molecular weight plus the mole fraction of the solute times its molecular weight.

From the molar polarization of the solute molecules the respective electric moments have been calculated. The results of these calculations are given in Table II. As in Table I, the symbols used are exactly those of the previous articles; they are, however, included to assist the reader. The quantity P_2'' is that part of the total polarization of the solute molecule

Table I

Dielectric Constant and Density Data for Substituted Phenols

o-Chlorophenol
Purified by fractional distillation under reduced pressure. B. p. 52–54° at 7 mm.

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.000	0.8735	2.276	26.66	75
0.9986	.8741	2.280	26.73	74
.9958	.8754	2.288	26.85	73
.9931	.8765	2.295	26.97	71.5
.9890	.8785	2.304	27.11	67.6
.9796	.8827	2.328	27.49	67.6
.9664	.8888	2.371	28.13	70.5

m-Chlorophenol
Purified by distillation under reduced pressure. M. p. 31–32°

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.000	0.8735	2.276	26.66	130
0.9986	.8741	2.286	26.81	136
.9944	.8759	2.314	27.24	130
.9903	.8778	2.343	27.67	130
.9864	.8798	2.371	28.07	130
.9796	.8827	2.418	28.75	129
.9730	.8859	2.463	29.38	128

p-Chlorophenol
Purified by fractional distillation under reduced pressure. M. p. 40–41°

1.000	0.8735	2.276	26.66	180
0.9986	.8741	2.289	26.86	170
.9958	.8751	2.314	27.24	164
.9931	.8764	2.331	27.49	148
.9890	.8783	2.364	27.97	146
.9796	.8826	2.435	29.00	141
.9664	.8888	2.545	30.50	141

o-Nitrophenol
Purified by distillation under reduced pressure. M. p. 44–45°

1.000	0.8735	2.276	26.66	235
0.9987	.8742	2.294	26.93	235
.9962	.8755	2.330	27.47	237
.9936	.8768	2.366	27.99	235
.9898	.8788	2.415	28.69	226
.9809	.8834	2.547	30.51	228
.9689	.8897	2.718	32.72	222

m-Nitrophenol
Purified by recrystallization from benzene. M. p. 96–97°

1.000	0.8735	2.276	26.66	345
0.9987	.8742	2.303	27.06	335
.9962	.8756	2.362	27.92	354
.9936	.8771	2.418	28.71	346
.9898	.8792	2.509	29.95	349
.9861	.8808	2.591	31.04	345

p-Nitrophenol
Purified by recrystallization from benzene. M. p. 113–114°

1.000	0.8735	2.276	26.66	563
0.9987	.8743	2.324	27.36	567
.9974	.8750	2.369	28.01	555
.9962	.8758	2.419	28.74	574
.9936	.8773	2.520	30.07	559

o-Bromophenol
Purified by fractional distillation. B. p. 189–191° (742 mm.)

1.000	0.8735	2.276	26.66	74
0.9990	.8744	2.280	26.73	..
.9969	.8762	2.285	26.81	74
.9948	.8781	2.291	26.92	76
.9918	.8807	2.300	27.05	74
.9867	.8852	2.314	27.29	74
.9798	.8913	2.332	27.59	73

p-Bromophenol
Purified by fractional distillation under reduced pressure. M. p. 64–65°

1.000	0.8735	2.276	26.66	206
0.9990	.8744	2.287	26.84	194
.9969	.8763	2.304	27.09	166
.9948	.8783	2.318	27.30	151
.9918	.8811	2.342	27.65	147
.9867	.8863	2.386	28.20	148
.9798	.8940	2.440	29.01	143

TABLE I (*Concluded*)

o-Anisidine[a]
B. p. 219–221° (742 mm.)

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.000	0.8735	2.276	26.66	83
0.9985	.8739	2.281	26.74	82
.9957	.8747	2.290	26.91	83
.9928	.8755	2.299	27.05	80
.9885	.8767	2.312	27.26	79
.9829	.8782	2.330	27.56	79

p-Anisidine[a]
M. p. 56–58°

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.000	0.8735	2.276	26.66	104
0.9985	.8739	2.283	26.78	106
.9957	.8748	2.296	26.99	104
.9928	.8755	2.310	27.21	102
.9885	.8769	2.331	27.54	103
.9829	.8786	2.360	27.98	104

m-Aminophenol
Purified by recrystallization from toluene. M. p. 123–124°

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.000	0.87354	2.276	26.66	101
0.99837	.87410	2.284	26.78	101

[a] The authors are indebted to Mr. C. F. Koelsch of our Division of Organic Chemistry for the preparation and purification of these compounds.

TABLE II

ELECTRIC MOMENT DATA FOR SUBSTITUTED PHENOLS

Molecule	P_2	P_2''	P_2'	$\mu \times 10^{18}$
o-C_6H_4OHCl	75	33	42	1.43
m-C_6H_4OHCl	130	33	97	2.17
p-C_6H_4OHCl	180	33	147	2.68
o-$NO_2C_6H_4OH$	235	33	202	3.10
m-$NO_2C_6H_4OH$	348	33	315	3.90
p-$NO_2C_6H_4OH$	563	33	530	5.05
o-BrC_6H_4OH	74	36	38	1.36
p-BrC_6H_4OH	206	36	170	2.86
o-$NH_2C_6H_4OCH_3$	83	37	46	1.50
p-$NH_2C_6H_4OCH_3$	104	37	67	1.80
m-$NH_2C_6H_4OH$	101	32	69	1.83[a]

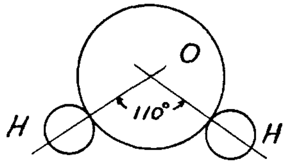
[a] This value was obtained from a single measurement in a very dilute solution and may, therefore, be subject to appreciable error.

caused by the deformation of the molecule, and is given by the quantity $\left(\frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M_2}{d}\right)$, (where n_D is refractive index for the "D" line at 25°); P_2' is that part of the total polarization of the solute molecule caused by its actual orientation in the field and is given by the quantity $\left(\frac{4\pi}{3} N \frac{\mu^2}{3kT}\right)$, where μ is the electric moment of the molecule and the remaining factors are constants.

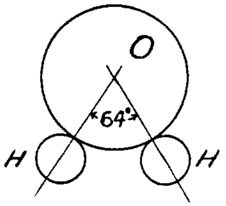
Discussion

There is now available ample evidence that an electric moment may be considered a characteristic property of a polar group. It is, in addition, a vector quantity, and as such there can be assigned to it both a magnitude and a direction, that is, an electrical character. For the latter purpose it is necessary arbitrarily to assign an electrical character to some one group. In the previous article of this series[10] it was possible to assign such a character to eight atoms or groups of atoms, making the simple assumption that the CH_3 group was positive. Included in a table presented in that article a negative character was assigned to the OH and OCH_3 groups, and it was the only character which could be assigned to these groups with the data available at that time. Shortly afterward it was found by one of us[11] that *p*-chlorophenol had a much larger electric moment than *o*-chlorophenol, indicating that in these particular compounds the OH group apparently was behaving as a positive rather than as a negative group, since there can be no question concerning the negative character of the chlorine atom. The manner in which these polarities have been assigned has been discussed in previous articles.[1,2,10] The assumptions underlying this treatment have been previously discussed and will not be repeated here. This method of assigning an electrical character to an atom or group is wholly satisfactory provided the group is simple in nature, but when the group which is substituted has attained any degree of complexity it may lead to difficulty for two reasons. (1) There may be an interaction between the groups. (2) It may be necessary to take into account the stereochemistry of the particular atom of the substituent group which is attached to the benzene (or other hydrocarbon) residue. Both of these factors have been previously recognized and described by one of us[4] and also independently by Höjendahl,[2] and subsequent work has only served to strengthen these conclusions, except that as the complexity of the molecule in question becomes greater, it is becoming increasingly difficult to separate these two effects.

In this article the second of these two factors is involved, since an oxygen atom is attached directly to the benzene nucleus. It is necessary first to consider the structure of the water molecule. An excellent summary of the available material has recently been given by Debye.[12] It is concluded that there are two possible models, both triangular in form, and, from the calculations given, the acute model is considered to be the more probable. The two possible models are reproduced below.



A



B

---

[10] Williams, This Journal, **50,** 2350 (1928).

[11] Williams, *Physik. Z.*, **29,** 683 (1928).

[12] Debye, "Polar Molecules," The Chemical Catalog Co., New York, **1929.**

It has already been suggested[1,4] that diethyl ether, methyl alcohol, anisole, the cresols, derivatives of the dihydroxybenzenes and other like oxygen derivatives are built up of structural oxygen units, differing only in the complexity of the group attached to the force fields ordinarily referred to as the valence bonds. In other words, all these compounds have structures similar to those given above for the water molecule. Such a structure, for example, appears to give the only adequate explanation for the fact that hydroquinone diethyl ether has a finite dipole moment.[4] In order to account for the electric moments of the substituted phenols given in Table II of this article, it is necessary as well to assume that they are derivatives of oxygen, rather than of benzene.

To predict the exact electric moment of molecules having such structures will not be an easy problem. The main difficulties appear to be: (1) the angle between the directions of the two valences of the oxygen atom is as yet uncertain and unobtainable. It is usually assumed to be 110°;[13] however, all that can be said with certainty is that it is less than 180°. Furthermore, there is every reason to believe that with two substituents on the same carbon atom they will either mutually repel each other if they are charged alike or will mutually attract each other if they are not charged alike. Very definite proof of such a mutual repulsion has been given for the case of two and three chlorine atoms attached to a single carbon atom,[14] and in this same article it is shown that like atoms or groups attached to adjacent carbon atoms mutually repel each other. Furthermore, it appears that this repulsion may even be exerted over a distance equivalent to four carbon atoms.

(2) In the case of the ortho and meta compounds it has been assumed by other investigators that there is free rotation of the benzene nucleus (with its substituted group) about the valence bond or shared electron pair. In any calculation which is made it will then be necessary to assign an equal probability to all possible positions about the circumference of the vector projected in a plane for the calculation. Such a procedure will limit the accuracy of any calculation, since it is very doubtful whether all possible positions of the rotation are equally probable under these circumstances.

The second difficulty in the calculation of the electric moment of an oxygen derivative does not apply in the case of a para-disubstituted hydroxy derivative of benzene. Thus Wolf[13] has been able to calculate the moments of *p*-cresol, *p*-cresyl methyl ether and *p*-chlorophenol with a reasonable degree of accuracy, making the assumptions that the OH is positive and that the angle between the two vectors characteristic of the two groups is always 110°.

Thus it appears desirable to consider molecules of the type under dis-

---

[13] Wolf, *Z. physik. Chem.*, **3B**, 128 (1929); Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929).

[14] Williams, *Z. physik. Chem.*, **138A**, 75 (1928).

cussion in this article as being built about an oxygen atom with its two valence bonds making an angle considerably less than 180° to each other, and to avoid assigning either a positive or a negative character to either the OH group or the OCH_3 group. Unpublished data of the authors for substituted anilines show that exactly similar difficulties are encountered in the case of the NH_2 group,[15] and that the electric moment data are most readily explained by considering these compounds to be derivatives of the ammonia molecule whose structure has been referred to in the introduction. These considerations are admittedly qualitative in character because one cannot as yet determine with any degree of security the magnitude of the angle which the various vectors make with each other.

The data of this article further emphasize the fact that equations such as those of Thomson[16] to calculate the electric moment of disubstitution products of benzene can be of use only in the case of substituent atoms or very simple substituent groups. If such atoms as carbon, oxygen and nitrogen are attached to the ring, a three-dimensional vector diagram must be considered because the valences of these atoms are directed in space rather than in a plane, so that when and only when the angles between these valence bonds become known with a reasonable degree of certainty will it be possible to calculate the electric moments of this type of molecule. In addition this calculation will be correct only when there is no interaction between the groups themselves, or when any such interaction between groups may be quantitatively accounted for. At present it appears that this interaction between groups is also of great significance.

Eucken and Meyer[17] have recently made the suggestion that in vectorial considerations of this sort it would be better to use values characteristic of linkages between atoms rather than to assign values to the atoms or groups of atoms themselves. One may at least maintain that such values are of no greater utility than the old ones, because they are calculated rather than observed by a direct experiment, and therefore involve questionable assumptions. This is particularly noticeable in the case of the values reported for the H—O and C—O linkages, both of which depend on an assumed angle between the two valence bonds of the oxygen. The electric moment for *p*-chlorophenol is calculated to be $\mu = 2.3 \times 10^{-18}$ e. s. u. We have been extremely careful with the determination of the electric moment of this molecule and find a value, $\mu = 2.68 \times 10^{-18}$ e. s. u. A value reported previously by one of us,[1a] $\mu = 2.4 \times 10^{-18}$ e. s. u., was found to have been slightly low because the dielectric constant and density data were not obtained for solutions containing less than 0.006 mole per cent. of *p*-chlorophenol in benzene solution.

[15] These data will be presented in a later communication.

[16] Thomson, *Phil. Mag.*, **46**, 513 (1923).

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

Summary

1. Electric moment data for a number of substituted phenols have been obtained by the method of the binary mixture. The dielectric constant and density data have been included.

2. The data have been discussed from the point of view of the stereochemistry of the oxygen atom.

3. It is shown that the dipole moment of a molecule can in general be calculated only provided the vectors characteristic of the groups be considered to be acting in *space*, for two reasons: (a) it is necessary to take into account the stereochemistry of the atoms forming the substituent group, and (b) it is necessary to take into account mutual attractions or repulsions between substituent groups unless they be separated by at least a distance equivalent to a chain of four carbon atoms, that is, by 5 Å.

4. Our knowledge is not at present sufficient to enable us to calculate with any degree of accuracy the electric moment of an "oxygen derivative."

MADISON, WISCONSIN

[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

THE COMPRESSIBILITY ISOTHERMS OF HYDROGEN, NITROGEN AND A 3:1 MIXTURE OF THESE GASES AT TEMPERATURES OF −70, −50, −25 AND 20° AND AT PRESSURES TO 1000 ATMOSPHERES

BY EDWARD P. BARTLETT, HARRY C. HETHERINGTON, HAMLINE M. KVALNES AND THOMAS H. TREMEARNE

RECEIVED NOVEMBER 16, 1929 PUBLISHED APRIL 7, 1930

This investigation was undertaken to provide data supplementing the earlier results obtained in this Laboratory on the compressibility of hydrogen, nitrogen and a 3 : 1 mixture of these gases at temperatures between 0 and 400° and at pressures to 1000 atmospheres.[1] The new data cover the temperature range −70 to 20°. They should be useful in the design of condenser equipment for synthetic ammonia plants and should be of especial interest in the study of equations of state for real gases.

Compressibility data in this temperature range dealing with hydrogen and nitrogen are already available.[1,2] However, at temperatures below 0°

---

[1] Bartlett, Cupples and Tremearne, THIS JOURNAL, **50**, 1275 (1928).

[2] (a) Natterer, *Pogg. Ann. Physik. Chem.*, **94**, 436 (1855); (b) Amagat, *Ann. chim. phys.*, [6] **29**, 68 (1893); (c) Witkowski, *Krakauer Anzeiger*, 305 (1905); (d) Kohnstamm and Walstra, *Proc. Roy. Acad.* (*Amsterdam*), 17, 203 (1914); (e) Schalkwijk, *Comm. Phys. Lab. Univ. Leiden*, No. 70; (f) Onnes, Crommelin and Smid, *ibid.*, No. 146b; (g) Holborn and Shultzer, *Ann. Physik*, **47**, 1089 (1915); (h) Smith and Taylor, THIS JOURNAL, **45**, 2107 (1923); (i) Smith and Taylor, *ibid.*, **48**, 3122 (1926); (j) Onnes and Penning, *Arch. Neerland. sci.*, IIIA, **6**, 277 (1923); (k) Crommelin and Swallow, *Comm. Phys. Lab. Univ. Leiden*, No. 172a (1924); (l) Onnes and van Urk, *ibid.*, No. 169d