

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## The Dipole Moments and Structures of the Esters of Some Fatty and Some Inorganic Acids

BY GEORGE L. LEWIS AND CHARLES P. SMYTH

This paper is a report of measurements of dipole moment made some time ago upon three groups of substances, all of which were esters. The moments of the ethyl esters of three long-chain fatty acids were determined with the object of confirming the expectation that the long chain would have little effect upon the moment. The moments of three alkyl borates were measured with the object of studying the structures of their molecules, in particular, the possibility of rotation around the B-O bonds. The moments of triphenyl phosphite, phosphate and thiophosphate were determined in the hope of obtaining further evidence as to the values of the moments of the semipolar bonds,  $P^+-O^-$  and  $P^+-S^-$ . The moments were obtained in the usual manner from measurements of the dielectric constants and densities of solutions in benzene or heptane. The dielectric constants were measured at a frequency of 520 kilocycles with a crystal-controlled heterodyne beat apparatus previously described,<sup>1</sup> and the densities were determined with an Ostwald-Sprengel pycnometer in a manner described elsewhere.<sup>2</sup>

### Purification of Materials

Benzene and heptane were purified as in previous work.<sup>3</sup> The ethyl undecylate, palmitate, and stearate were portions of the materials which had been carefully purified by Dr. W. O. Baker in this Laboratory for use in studying the dielectric constants in the solid state.<sup>4</sup>

The three alkyl borates were prepared by Dr. Allen Scattergood by fractionating a mixture of two moles of boric acid and nine moles of the corresponding alcohol according to the method given in "Organic Syntheses."<sup>5</sup> The liquids had the following values of the boiling point, the density  $d$ , the refractive index for the sodium D line  $n_D$ , and the dielectric constant  $\epsilon$  at 25°: *n*-propyl borate, b. p. 177-178°,  $d$  0.85448,  $n_D$  1.39227,  $\epsilon$  2.239; *i*-butyl borate, b. p. 208.0-208.5°,  $d$  0.84033,  $n_D$  1.40101,  $\epsilon$  2.213; *s*-butyl borate, b. p. 193-194°,  $d$  0.82902,  $n_D$  1.39444,  $\epsilon$  2.194.

**Triphenyl Phosphite.**—Material from the Eastman Kodak Company was washed with dilute sodium carbonate solution and then with water, dried over calcium chloride,

filtered, and vacuum distilled at 200° and 6 mm.;  $n_D^{25}$  1.58801.

**Triphenyl Phosphate.**—Material from the Eastman Kodak Company was recrystallized from distilled ether three times; m. p. 46°.

**Triphenyl Thiophosphate.**—Material from the Eastman Kodak Company was recrystallized from distilled ether three times; m. p. 53°.

### Experimental Results

The dielectric constants,  $\epsilon$ , and the densities,  $d$ , of benzene or heptane solutions containing mole fraction  $c_2$  of solute are given in Table I, the polarizations  $P_2$  being listed in the last column. The polarization of the pure solvent is given as  $P_1$ . Table II lists in the second column the values of  $MR_D$ , the molar refraction for the D sodium line, obtained directly from the experimental data for the long chain esters and the borates, and calculated for the phosphite, phosphate and thiophosphate from the refractions of the corresponding alkyl compounds,<sup>6</sup> the refraction of benzene, and atomic refractions given in Landolt-Börnstein. The third column gives the polarizations  $P_2$  for the pure liquids at 25°, the fourth column the polarizations  $P_\infty$  obtained by extrapolation to  $c_2 = 0$  of the values of  $P_2$  in Table I, and the fifth column gives the dipole moments calculated in the usual manner.

### Discussion of Results

For the long-chain esters of the fatty acids in Table II the difference between the polarization of the pure liquid and that of the substance at infinite dilution decreases with increasing length of the carbon chain; the difference being 25.0 for ethyl undecylate, 17.8 for ethyl palmitate, and 15 for the stearate, for which the difference is obtained by a rough extrapolation of the polarization of the pure liquid down to 25°. Increase in the length of the chain effectively dilutes the dipoles and thereby reduces the intermolecular action, which is responsible for the difference between  $P_2$  and  $P_\infty$ . This difference is very small in the three alkyl borates as it is in ethyl ether<sup>7</sup> and for the same reason. The three ethyl groups form a shield around the three C-O moments, while, as will be seen presently, the three B-O dipoles radiating from the center of the molecule presumably cancel one another. The variation of  $P_2$  with concentration for triphenyl phosphite in Table I is much less than that in the cases of the

(1) Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

(2) Lewis and Smyth, *THIS JOURNAL*, **61**, 3063 (1939).

(3) Smyth and Walls, *ibid.*, **54**, 1854 (1932).

(4) Baker and Smyth, *ibid.*, **60**, 1229 (1938).

(5) "Organic Syntheses," W. H. Carothers, Ed., Vol. XIII, John Wiley and Sons, New York, N. Y., 1933, p. 16.

(6) Jones, Davies and Dyke, *J. Phys. Chem.*, **37**, 583 (1933).

(7) *Trans. Faraday Soc.*, **30**, Appendix (1934).

TABLE I  
 DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS AT  
 25°

$\epsilon_0$	$\epsilon$	$d$	$P_2$
Heptane-Ethyl Undecylate			
0.00000	1.917	0.67958	(34.49 = $P_1$ )
.02389	1.984	.68696	135.5
.05707	2.063	.69705	131.3
.07051	2.093	.70098	129.6
.08980	2.132	.70558	127.8
Heptane-Ethyl Palmitate			
0.00659	1.936	.68250	160
.01883	1.966	.68736	157
.02863	1.997	.69091	156
.03106	1.999	.69196	155
.04063	2.024	.69566	155
.06051	2.073	.70307	153.4
.08181	2.121	.71070	151.7
.11265	2.191	.72068	149.8
.15184	2.259	.73206	147.9
Heptane-Ethyl Stearate			
0.02063	1.974	.68833	166
.04154	2.028	.69724	163.5
.06501	2.082	.70642	161.2
.08909	2.128	.71518	159.4
.11978	2.177	.72329	157.4
Benzene- <i>n</i> -Propyl Borate			
0.00000	2.276	.87344	(26.67 = $P_1$ )
.04864	2.273	.87091	64.9
.08467	2.272	.86918	65.0
.13320	2.266	.86709	64.6
Benzene- <i>i</i> -Butyl Borate			
0.03237	2.275	.86990	81.2
.07196	2.273	.86554	80.9
.10729	2.267	.86235	80.9
Benzene- <i>s</i> -Butyl Borate			
0.03860	2.273	.86851	81.4
.06912	2.270	.86453	81.5
.09238	2.265	.86115	81.3
Benzene-Triphenyl Phosphite			
0.01423	2.359	.88568	170.8
.02988	2.461	.89905	170.6
.04001	2.525	.90773	170.5
.05302	2.605	.91887	170.1
.06389	2.674	.92819	169.6
Benzene-Triphenyl Phosphate			
0.02098	2.517	.89341	246.9
.03210	2.645	.90389	245.4
.05142	2.867	.92226	242.7
.06831	3.061	.93830	239.7
.08354	3.236	.95276	237.3
Benzene-Triphenyl Thiophosphate			
0.01035	2.378	.88425	227.4
.02770	2.544	.90238	223.8
.03372	2.598	.90866	222.9
.04010	2.657	.91533	220.7
.05328	2.779	.92910	218.8

 TABLE II  
 MOLAR REFRACTIONS, POLARIZATIONS (AT 25°) AND DI-  
 POLE MOMENTS

Substance	$M_{RD}$	$P_2$	$P_\infty$	$\mu \times 10^{18}$
$C_{10}H_{21}COOC_2H_5$	63.8	113.1	138.1	1.89
$C_{15}H_{31}COOC_2H_5$	87.08	141.6	159.4	1.87
$C_{17}H_{35}COOC_2H_5$	95.91	146.6 (42°)	168.8	1.88
$(n-C_2H_7)_3BO_3$	52.55	64.30	65.0	0.77
$(i-C_4H_9)_3BO_3$	66.44	78.81	81.5	.85
$(s-C_4H_9)_3BO_3$	66.44	78.95	81.4	.85
$(C_6H_5)_3PO_3$	87.2		171.7	2.02
$(C_6H_5)_3PO_4$	86.1		250	2.81
$(C_6H_5)_3PO_3S$	93.3		231	2.58

phosphate and thiophosphate, which indicates that the P-O and C-O moments are well screened by the phenyl groups in the former, while the large  $P^+-O^-$  and  $P^+-S^-$  dipoles in the latter two give rise to strong intermolecular action.

The moments of ethyl undecylate, palmitate and stearate in Table II may be regarded as identical. They are also identical with the value 1.86 found in this Laboratory for ethyl acetate in benzene solution<sup>8</sup> but lower than the value 1.98 for ethyl acetate in heptane.<sup>9</sup> In general, the moments of a large number of esters in the literature show an increase in value from the methyl to the ethyl, presumably because of induction, with little change produced by further lengthening of this part of the molecule. On the other side of the molecule, addition of carbon to go from formate to acetate to propionate lowers the moment slightly as it lowers the dissociation constant, the latter to a much greater extent. The moments of these three long-chain ethyl esters are only 0.05 higher than the values for ethyl propionate<sup>8,10</sup> and butyrate<sup>10</sup> in benzene solution, a difference to be expected from the difference in solvent effect. It may, therefore, be concluded that the long chains in these molecules do not affect the dipole moment of the molecule or hinder its free orientation in externally applied electric fields of frequencies up to those employed in the present measurements.

The moment of propyl borate in Table II fits well into the series of values 0.75, 0.77 and 0.79 previously found for ethyl borate,<sup>11</sup> butyl borate,<sup>12</sup> and amyl borate,<sup>12</sup> respectively. The branching of the carbon chain seems to raise the moment slightly, the isobutyl and *s*-butyl borate moments in Table II being 0.85. In view of the zero mo-

(8) Smyth and Walls, *THIS JOURNAL*, **53**, 527 (1931).

(9) Smyth, Dornte and Wilson, *ibid.*, **53**, 4242 (1931).

(10) Wolf and Gross, *Z. physik. Chem.*, **B14**, 305 (1931).

(11) Cowley and Partington, *Nature*, **136**, 643 (1935).

(12) Otto, *THIS JOURNAL*, **57**, 1476 (1935).

ment found for boron trichloride<sup>7</sup> and the symmetrical, triangular planar structures found by electron diffraction for the boron halides and boron trimethyl<sup>13</sup> and the analogous symmetrical structure found by X-ray analysis for the  $\text{BO}_3$  group in crystalline boric acid and metallic metaborates<sup>14</sup> it seems almost certain that, in these alkyl borates, the boron lies at the center of an equilateral triangle with the oxygens at the three apices. As the resultant of the three B-O moments would thus be zero, any moment of the molecule as a whole must be due to the H-C and C-O bond moments. The total R-O moment may be taken as approximately 1.2 acting in the C-O direction.<sup>15</sup> If all positions of rotation around the B-O bonds were equally probable and if the oxygen valence angle were  $110^\circ$ , the resultant moment of the trialkyl borates should be<sup>16</sup>  $1.2\sqrt{3} \sin 110^\circ = 1.95$ . However, the borates should have structures which through resonance are mainly the resultant of contributions from three structures such as  $\text{RO}-\overset{\text{OR}}{\underset{\text{OR}}{\text{B}}}$ . Conse-



quently, the B-O should have approximately one-third double-bond character, which would tend to make the three carbons attached to the three oxygens coplanar with the boron and the oxygens and give oxygen valence angles of about  $120^\circ$ . If steric repulsion between the alkyl groups were negligible, there would be eight possible coplanar arrangements of the three alkyl groups, six of them equivalent to one another and having a moment 2.1 and the remaining two being equivalent to one another and having zero moment. The resultant observed moment should then be  $2.1\sqrt{6/8} = 1.8$ . Increase of the oxygen valence angles to a rather probable value of  $125^\circ$  would decrease this calculated value by 0.1. The observed values in Table II are less than half of these calculated values.

Examination of the bond and kinetic theory radii of the atoms in these molecules shows that neglect of steric repulsion in calculating moments for the molecules is quite unjustifiable. In the hypothetical structure in which free rotation is supposed, the positions in which the alkyl groups turn on to the same side of the molecule, thereby

giving the maximum resultant moment, are rendered much less probable by repulsion between the groups. The resulting tendency to occupy positions giving lower resultant moment could account for the difference between the low observed and the high calculated moment values. In the more probable structure in which partial double-bond character hinders or prevents rotation around the B-O bonds, steric repulsion renders the six equivalent, unsymmetrical, planar structures impossible or highly improbable without distortion. The distortion and greatly decreased probability of these structures of large moment and the greatly increased probability of the two symmetrical structures of zero moment, in which steric repulsion is small or negligible, can easily account for the smallness of the observed moments.

The conclusion that steric repulsion is the cause of the low moments of the alkyl borates is borne out by examination of the moment values, 1.85 and 1.90, found by Otto<sup>12</sup> for butylboric and amylboric acids, respectively. If the H-O moment is taken<sup>15</sup> as 1.5, the moment calculated as before for the hypothetical structure having freedom of rotation around the B-O bonds is 2.35 and the value calculated for the planar structure without rotation around the B-O bonds is about 2.1. As there is only one alkyl group in these molecules, steric repulsion should be very much less than that in the trialkyl borates. Indeed, of the eight possible arrangements in the planar structure, the two equivalent ones having largest moment should have almost as little steric repulsion as the two with smallest moment, only the dipole-dipole interactions reducing somewhat the probabilities of the former two. The observed value 1.9 is thus reduced but slightly below the roughly calculated value 2.1. The observed moments of the trialkyl borates and the monoalkyl boric acids are evidently consistent with the planar structure in which the three B-O bonds making angles of  $120^\circ$  with one another have sufficient double-bond character to prevent rotation around the bonds, although, in the so-called unsymmetrical planar structure, steric effects would tend to twist the carbons attached to the oxygens out of the plane of the boron and the oxygens. The moment values alone do not, however, preclude the possibility of rotation around the B-O bonds.

The triphenyl phosphite molecule looks some-

(13) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, pp. 88, 220.

(14) Ref. 13, pp. 195, 291.

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

(16) See Eyring, *Phys. Rev.*, **39**, 746 (1932); Smyth and Walls, *This Journal*, **54**, 2261 (1932).

what analogous to those of the alkyl borates, but the moment observed for it is more than twice as large. If all positions of rotation around the C-O and P-O moments were equally probable, its mean square moment could be written<sup>16</sup>  $\mu_1^2 = 3m_1^2(1 + 2\cos^2\theta\cos\varphi) + (3m_2^2 + 6m_1m_2\cos\theta)(1 + 2\cos\varphi)$ , in which  $m_1$  is the sum of the H-C and C-O bond moments,  $m_2$  is the P-O bond moment,  $\theta$  is the oxygen valence angle, and  $\varphi$  is the phosphorus valence angle. The same equation was used to calculate the moment of the alkyl borates, for which the fact that  $\varphi$  was  $120^\circ$  caused all the terms containing  $m_2$ , the B-O moment, to drop out.  $m_1$  is calculated<sup>15</sup> from the moment of diphenyl ether 1.14 as 1.0, and  $m_2$  is calculated as the difference 1.2 between the H-O and H-P bond moments.<sup>15</sup> The oxygen valence angle  $\theta$  is taken as  $110^\circ$  as in the borates. The phosphorus valence angle is  $100^\circ$  in trimethylphosphine and varies from  $98^\circ$  to  $104^\circ$  in the phosphorus trihalides.<sup>17</sup> If it is taken as  $100^\circ$  in triphenyl phosphite, the moment calculated by the above equation is 2.0, in exact agreement with the observed value in Table II. Increase of the angle  $\varphi$  to  $110^\circ$  reduces the calculated value to 1.8 and further increase to  $120^\circ$  reduces it to 1.6. In spite of the excellent agreement between the observed and calculated moment values, examination of the atomic dimensions shows that certain positions of rotation around the P-O bonds are impossible because of interference of the benzene rings with one another. There is, however, no general exclusion of the positions of highest moment like that which lowers the moment so much in the case of the borates. A sufficiently wide variety of positions appears to be possible to permit of a distribution of moment values close to the random one given by the equation. If, instead of using the estimated value 1.2 for the single P-O bond moment to calculate the resultant moment of the triphenyl phosphite molecule, the observed moment of the molecule is used to calculate the P-O moment, the value obtained is 1.2, which may therefore be regarded as an approximate experimental value for the normal P-O bond.

The moments of the phosphate and thiophosphate molecules are changed from that of the phosphite by the presence of the semipolar bond  $P^+-O^-$  or  $P^+-S^-$  and the calculated mean square moment should be

(17) See ref. 13, p. 80.

$$\mu_2^2 = \mu_1^2 + m_3^2 + 6m_2m_3\cos\chi + 6m_1m_3\cos\theta\cos\chi$$

where  $\mu_1$  is the moment of the phosphite as given by the previous equation for it,  $m_2$  is the semipolar bond moment,  $\chi$  is the angle which the semipolar bond makes with the three P-O bonds, and the other quantities are the same as those used in the previous equation. In the case of the phosphite, the most probable value of the O-P-O angle,  $\varphi = 100^\circ$ , gives exact agreement between the observed and calculated moments. If  $\varphi = 100^\circ$  in the phosphate and thiophosphate, then the O-P<sup>+</sup>-O<sup>-</sup> angle  $\chi$  may be calculated as  $118^\circ$ , since the P<sup>+</sup>-O<sup>-</sup> or P<sup>+</sup>-S<sup>-</sup> bond should lie symmetrically with respect to the three P-O bonds. When  $\mu_2$  is set equal to the observed moment for the phosphate or thiophosphate in Table II and  $\mu_1$  is taken as the observed phosphite moment, which agrees with the calculated value, the moment  $m_3$  of the semipolar P<sup>+</sup>-O<sup>-</sup> bond is given by the equation as 3.5 and that of the P<sup>+</sup>-S<sup>-</sup> bond as 3.2. If all the phosphorus valence angles were identical so that  $\chi = \varphi = 110^\circ$ ,  $\mu_1$  would have the calculated value 1.83, and the values of  $m_3$  calculated would be 3.2 for the P<sup>+</sup>-O<sup>-</sup> bond and 2.9 for the P<sup>+</sup>-S<sup>-</sup> bond. As the first structure, in which  $\varphi = 100^\circ$  and  $\chi = 118^\circ$ , seems to be the most probable approximation, the values 3.5 for P<sup>+</sup>-O<sup>-</sup> and 3.2 for P<sup>+</sup>-S<sup>-</sup> should be most nearly correct. It should be borne in mind, however, that, as in the previously considered<sup>18</sup> case of the same bonds in POCl<sub>3</sub> and PSCl<sub>3</sub>, neither bond is a pure semipolar structure, as other resonating forms, particularly double-bonded structures, contribute to the structures of the molecules. The values must, in any event, be regarded as approximate because of possible errors in the assumed bond moments and valence angles. The P<sup>+</sup>-O<sup>-</sup> moment value 3.5 is identical with that found for this bond in POCl<sub>3</sub>, while the value 3.2 for the P<sup>+</sup>-S<sup>-</sup> bond is considerably higher than the apparent value 2.5 found for it in PSCl<sub>3</sub>, which was thought to be too low because of the inductive action of the P-Cl dipoles. The small difference 0.3 here found between the P<sup>+</sup>-O<sup>-</sup> and P<sup>+</sup>-S<sup>-</sup> moments justifies the conclusion previously reached<sup>18</sup> that the two moments are not very different from one another, the two lying in the neighborhood of 3.5, where most of the more or less hybrid semipolar bonds seem to lie. It would appear that the P<sup>+</sup>-S<sup>-</sup> is actually some-

(18) Smyth, Lewis, Grossman and Jennings, *THIS JOURNAL*, **62**, 1219 (1940).

what lower than the  $P^+-O^-$  moment in contrast to the fact that the  $C=S$  moment is 0.3 higher than the  $C=O$ , which latter bonds contain large contributions from semipolar forms.<sup>19</sup>

### Summary

The dielectric constants and densities of solutions of ethyl undecylate, palmitate and stearate in heptane, of *n*-propyl, *i*-butyl and *s*-butyl borate in benzene, and of triphenyl phosphite, phosphate and thiophosphate in benzene have been measured at 25° and used to calculate the dipole moments of the molecules of the solutes.

The small variation of polarization with concentration shows the intermolecular action to be very small in the three trialkyl borates and in triphenyl phosphite and to decrease with increasing molecular size in the long-chain fatty acid esters. The small intermolecular action is due to effective screening of the dipoles from one another by the hydrocarbon groups, while the large intermolecular action in the phosphate and thiophosphate is due to the presence of an imperfectly screened semipolar bond.

(19) Smyth, *THIS JOURNAL*, **60**, 183 (1938).

Ethyl undecylate, palmitate and stearate have dipole moments indistinguishable from one another and from those of ethyl propionate and butyrate, which shows that the long chains in these molecules do not affect the dipole moment of the molecule or hinder its free orientation at 25° in an alternating electric field of frequency as high as 520 kc. Equations are derived for the calculation of the resultant moments of the trialkyl borates and of triphenyl phosphite, phosphate and thiophosphate on the assumption of equal probabilities of all the positions of rotation around the B-O and P-O bonds. Strong steric repulsion between the alkyl groups in the borates lowers their moments to less than half of the values calculated on the basis of free rotation as well as on that of B-O bonds stiffened by double-bond character. Excellent agreement is obtained between the observed and the calculated values for triphenyl phosphite, where steric hindrance plays a minor role. The equations are used to calculate approximate moment values for three bonds as follows: P-O, 1.2;  $P^+-O^-$ , 3.5;  $P^+-S^-$ , 3.2.

PRINCETON, NEW JERSEY

RECEIVED APRIL 12, 1940

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 762]

## A Redetermination of the Parameters in Ammonium Bifluoride

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### Introduction

The structure of ammonium bifluoride has been determined by Pauling,<sup>1</sup> who gave approximate values of the parameters obtained with the use of the data of Hassel and Luzanski.<sup>2</sup> He found a hydrogen-bonded structure with each nitrogen atom surrounded by four fluorine atoms at tetrahedral corners, the mean N-F distance being  $2.76 \pm 0.06$  Å. and the F-F distance  $2.37 \pm 0.10$  Å. The value we have found<sup>3</sup> for the F-F distance in  $KHF_2$ ,  $2.26 \pm 0.01$  Å., is equal to Pauling's value of the distance in  $NH_4HF_2$  to within its limits of error, so it is not possible to say whether or not the distance has been increased by the formation of two additional hydrogen bonds in  $NH_4HF_2$ . For this reason a more accurate determination of this distance has been made.

(1) L. Pauling, *Z. Krist.*, (A) **85**, 380 (1933).

(2) O. Hassel and N. Luzanski, *Z. Krist.*, **83**, 448 (1932).

(3) L. Helmholtz and M. T. Rogers, *THIS JOURNAL*, **61**, 2590 (1939).

The unit translations found by Hassel and Luzanski<sup>2</sup> and the parameters given by Pauling<sup>1</sup> have been revised and the limits of error reduced. From these new values the F-F and N-F distances have been calculated to be  $F-F = 2.32 \pm 0.03$  Å. and  $N-F = 2.82 \pm 0.03$  Å. The weakening of the F-F bond in the formation of two hydrogen bonds in passing from  $KHF_2$  to  $NH_4HF_2$  is thus shown to exist; the increase in bond length amounts to  $0.06 \pm 0.04$  Å. The space group  $D_{2h}^7$  used by Pauling has been confirmed by the absence of reflections of the type  $(h0l)$ ,  $h$  odd, observed by Hassel and Luzanski.

### Experimental Method and Results

Oscillation photographs about the  $c$  and  $a$  axes were taken of crystals of orthorhombic  $NH_4HF_2$  prepared by evaporation of solutions of  $NH_4HF_2$  in glacial acetic acid.

The space group was shown to be  $D_{2h}^7$  by the