Tetranitrophenylmethylnitramine was synthesized using pure dinitrodimethylaniline. To a flask containing 500 ml. of nitric acid (d. 1.52; distilled from dry potassium nitrate and sulfuric acid) cooled to −5° was added 40 g. (0.19 mole) of 3,5-dinitrodimethylaniline during the course of 45 min. The temperature was kept below 0° during the addition. The nitration mixture was allowed to come gradually to room temperature and then to stand for at least 16 hr. The nitric acid solution was again cooled to 0° while approximately 200 ml. of ice-cold distilled water was added. The nitramine, which precipitated as a finely-crystalline light buff-yellow powder, was separated by filtration, dried and recrystallized from dry, warm ethylene dichloride. The yield of product melting at 131–132° (dec.) was 31.5 g. (50%). *Anal.* Calcd. for $C_7H_4N_6O_{10}$: C, 25.31; H, 1.21; N, 25.31. Found: C, 25.50, 25.42, 25.42; H, 1.41, 1.38, 1.35; N, 25.49. Found by Blanksma[3]: N, 25.8.

2,3,4,6-Tetranitrophenylmethylnitramine was obtained in the manner of Blanksma[3] from *m*-nitroaniline by methylation followed by nitration. In a typical experiment 28 g. (0.2 mole) of *m*-nitroaniline was added slowly to a stirred suspension of 88 g. (0.7 mole) of dimethyl sulfate in 125 ml. of water. During the addition and subsequent stirring at room temperature (reaction time 2 hr.) solid soda ash was added as necessary to keep the solution basic to phenolphthalein. At the conclusion of the reaction, the mixture was heated to 50° and additional alkali added to destroy excess dimethyl sulfate.

The dark red solid which appeared upon cooling was filtered, and purified by steam distillation to separate it from a small amount of non-volatile material. About 3 l. of distillate was collected, from which was obtained 15 g. (45%) of *m*-nitrodimethylaniline melting at 51–59°.

Attempted N-methylation of *m*-nitroaniline by the method of Clarke[14] which had been successful with dinitroaniline gave here 2,2'-dinitro-4,4'-bis-(dimethylamino)-diphenylmethane, m.p. 191–193°, as the major product, already described by Ullmann and Maric[15] as melting at 195°.

The nitration was performed by adding 53 g. (0.32 mole) of *m*-nitrodimethylaniline to 660 ml. of 100% nitric acid during a period of one hour, maintaining the stirred solution at 0°. The product was isolated after standing at room temperature for 24 hours by adding water at 10°. The solid which separated was recrystallized from ethylene chloride to give 53 g. (50%) of 2,3,4,6-tetranitrophenylnitramine melting at 145–146° (dec.).

2,3,4,6-Tetranitroaniline was made by the nitration of *m*-nitroaniline using sulfuric and nitric acids essentially in the manner described by Flurscheim[16] who first prepared it.

Picramide was obtained by synthesis from ammonia and picryl chloride, after the manner described for 2,4-dinitroaniline.[17] It was recrystallized from glacial acetic acid for purification.

(15) F. Ullmann and A. Maric, *Ber.*, **34**, 4315 (1901).

(16) B. Flurscheim, *Z. ges. Schiess, u. Sprengstoffw.*, **8**, 185 (1913); *J. Soc. Chem. Ind.*, **40**, 97 (1921).

(17) F. B. Wells and C. F. H. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 221; see also Beilstein, **12**, 763 (1929).

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Determination of the Dipole Moments of Some Derivatives of Hydroxybenzoic Acid[1]

BY CHARLES S. COPELAND AND M. WESLEY RIGG

The dipole moments of several salicylate esters are reported, some of which disagree with previously published values. The dipole moments of a number of additional compounds (recalculated from the original references and compared with the reported values) have been used to calculate a value for the dipole moment of the salicylate esters from group moments. It was found that it is not possible to determine structure in all cases by the use of dipole data. The molecule diethoxymethane was found to exhibit hindered rotation about the O–C–O group. It is shown that small systematic errors in experimental work do not cause a serious error in the calculated value of the dipole moment provided the calculation is made according to the methods discussed.

The effect of hydrogen bonding upon the dipole moment of hydroxy and methoxy benzoic acid esters is of interest since the moment calculated from group values does not agree with the values which have been reported for the salicylate esters.[2] It was also noted[3] that there is generally only a small change in the value of the moments with increase in molecular weight in a homologous series, *i.e.*, the substitution of ethyl or propyl for a methyl group. However, a considerable variation in the reported moments for the salicylate esters was noted. Furthermore, unlike the other phenyl derivatives, the moment of phenyl salicylate is higher than similar derivatives in other compounds. The variation in the values (reported by a number of investigators) for the same compound is also large.

The purpose of this investigation was to verify the reported values of the dipole moments of the salicylate esters, and to determine the dipole moments of a number of additional hydroxy and methoxy benzoates.

(1) Presented before the 110th Meeting of the American Chemical Society, September, 1946, in Chicago, Illinois.

(2) C. Hyrnakowski and C. Kalinowski, *Compt. rend.*, **197**, 483 (1933).

(3) Symposium on Dipole Moments, *Trans. Faraday Soc.*, appendix (1934).

Experimental

Dielectric constants were determined by the resonance method, using a frequency of 1200 kilocycles. *Capacitances* were obtained using a General Radio Precision variable condenser (type 772D) in parallel with the experimental condenser consisting of three concentric gold-plated brass cylinders held apart by Pyrex wedges, the inner and outer cylinders being connected by gold-plated brass screws. Its capacitance was found in a series of 28 calibrations over a period of a year to be 50.634 ± 0.77 mmf. *Densities* were obtained by weighing a calibrated glass bob both in air and in the thermostated substance in question with an analytical balance. *Refractive indices* were measured with an Abbe refractometer.

Preparation and Purification of Materials.—*Benzene* was washed with concentrated sulfuric acid, and then with water, dried, and finally fractionally recrystallized three times. It was stored over sodium and distilled off immediately before use. *Methyl, ethyl* and *isopropyl salicylates* and *ethyl benzoate, phenyl salicylate* and *methyl p-hydroxybenzoate* were obtained from the Eastman Chemical Co. The first four materials were fractionally distilled under reduced pressure when needed, the middle, constant-boiling fractions being collected and found to contain neither water nor free acid. The last two materials were fractionally crystallized from their melts and then recrystallized from benzene to constant melting points. *Methyl o-methoxybenzoate* and *methyl p-methoxybenzoate* were prepared by treating methyl salicylate or, respectively, methyl p-hydroxybenzoate with methyl sulfate in benzene solution and refluxing for several hours. The mixture was washed successively with sodium bicarbonate and dilute sodium hydroxide solutions,

TABLE I

COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES

Compound	$n_D{}^a$	d^a	$R_D{}^b$	$R_D{}^c$	Melting points, t, °C.		
					Eastman product	Purified product	Beilstein
Methyl salicylate	1.535	1.178	40.17	38.72			
Ethyl salicylate	1.523	1.046	44.85	43.34			
Isopropyl salicylate	1.509	1.079	49.87	47.96			
Phenyl salicylate	1.579	1.178	60.40	58.21	41.5–42.4	41.8^e–42.6^d	42–43
Methyl p-hydroxybenzoate					125.6–162.6	126.0–126.6^a	131
Ethyl p-hydroxybenzoate					115.8–116.6	116.0–116.6^d	116
Methyl p-methoxybenzoate	1.534	1.119	45.40	43.46		48.2^e	45–47
Methyl o-methoxybenzoate						98.0– 98.5	98–100
Diethoxymethane	1.373	0.8280	28.62	28.58			
Ethyl benzoate	1.505	1.132	42.57	41.82			

^{a} The density and the refractive index were both measured at the same temperature. ^{b} Experimental molar refraction. ^{c} Calculated from atomic refractions. ^{d} Capillary melting point. ^{e} Melting point obtained from the cooling curve of a large sample.

and with water, and was then dried over anhydrous sodium sulfate. After distilling off the benzene, the residue was distilled under reduced pressure. *Diethoxymethane* was prepared from formaldehyde and ethyl alcohol in the presence of a trace of sulfuric acid. The resulting lighter phase, containing the product in dilute alcohol and water, was washed with sodium carbonate and then dried over a large quantity of calcium chloride to avoid the formation of a minimum-boiling, azeotropic mixture. The product, after drying, was fractionally distilled and the middle constant-boiling fraction collected and used. The physical properties of the various materials are shown in Table I.

The *molar polarization* of a solute at infinite dilution in a non-polar solvent was calculated by the use of equation (1),[4] where M_1 and M_2 are the

$$P_{20} = \frac{3M_1a}{(\epsilon_1 + 2)^2 d_1} \left(\frac{M_2}{d_1} - \frac{bM_1}{d^2_1}\right)\left(\frac{\epsilon_1 - 1}{\epsilon_1 + 2}\right) \quad (1)$$

molecular weights of solvent and solute, respectively, and ϵ_1, d_1, a, and b are defined by the equations

$$\epsilon_{12} = \epsilon_1 + aN_2 \qquad d_{12} = d_1 + bN_2 \quad (2)$$

where ϵ_{12} and d_{12} are the measured dielectric constant and density of a solution of mole fraction N_2 of solute.

The values of ϵ_1 and d_1 in equations (2) (from a least squares solution) should be the values for the pure solvent. Appreciable deviation is evidence of an error.

It is interesting to know to what extent the above method eliminates the effect of systematic errors on the value of P_{20}. Two errors are considered: the error introduced by contamination of the solvent and the error caused by the use of an incorrect value of the replaceable capacitance of the experimental condenser and/or the glass bob used in determining densities.

To determine the effect of the first: Two series of solutions of ethyl benzoate in benzene were prepared using in one, purified benzene, and in the other unpurified commercial benzene containing thiophene. The results are shown in Table II and Fig. 1.

TABLE II

Solvent, benzene	ϵ_1	d_1	a	b	P_{20}
Pure	2.273	0.8730	5.586	0.2707	125
Impure	2.279	.8719	5.384	.2727	122

(4) G. Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929); I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).
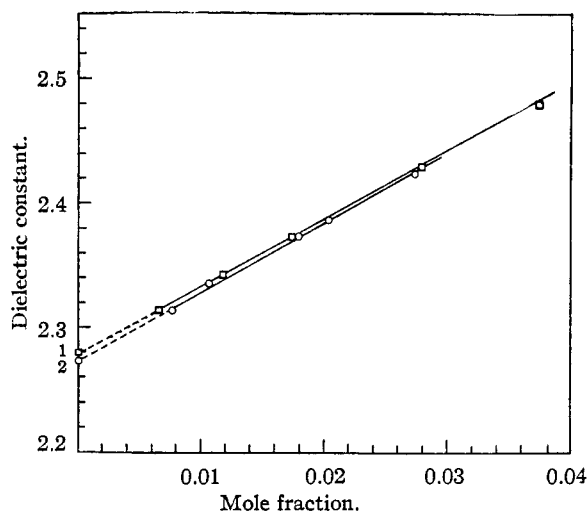

Fig. 1.—Ethyl benzoate: 1, □, impure benzene; 2, O, pure benzene.

The values of P_{20} are in good agreement. For comparison, Fig. 2 shows the molar polarization,
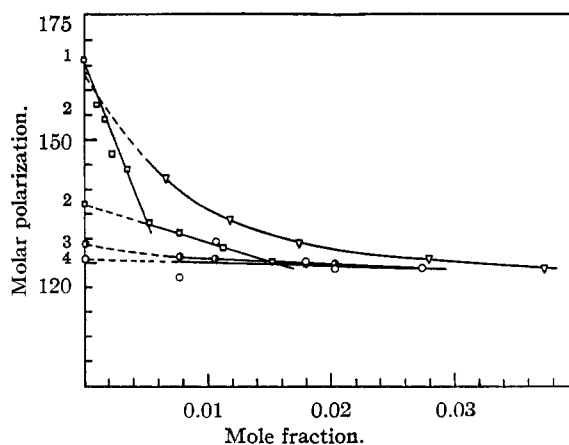

Fig. 2.—Ethyl benzoate:

		Ref. 6, □, 2	∇, 1	This paper O, 3	◐, 4
Solvent	....	Imp. Bz	Pure Bz	Pure Bz	smoothed
P_{20}		133	166	160	126	128
μ		2.14	2.43	2.40	2.02	2.03

TABLE III

SUMMARY OF THE DIPOLE MOMENTS AND THE CONSTANTS REQUIRED FOR THE CALCULATION OF THE DIPOLE MOMENT

Compound	M_2	ϵ_1	a	d_1	b	P_∞	$1.05R_D$	P_μ	μ
Methyl salicylate	152.14	2.274	9.077	0.8735	0.4117	172.7	40.66	132.0	2.53
Ethyl salicylate	166.16	2.273	10.08	.8730	.3972	192.7	45.51	147.2	2.69
Isopropyl salicylate	180.20	2.264	10.81	.8727	.3624	209.8	50.36	159.4	2.78
Phenyl salicylate	214.21	2.275	7.880	.8734	.6141	170.7	61.12	109.6	2.27
Methyl p-hydroxybenzoate	152.14	2.268	11.87	.8724	.5703	209.5	40.66	168.8	2.87
Ethyl p-hydroxybenzoate	166.17	2.271	12.00	.8730	.5067	218.0	45.51	172.5	2.90
Methyl p-methoxybenzoate	166.08	2.264	9.460	.8727	.4348	185.8	45.63	140.2	2.62
Methyl o-methoxybenzoate	166.08	2.265	11.37	.8729	.4599	210.2	45.63	164.6	2.84
Diethoxymethane	104.09	2.268	0.5387	.8717	.0549	41.67	30.01	21.36	0.75
Ethyl benzoate	150.17	2.273	5.586	.8730	.2707	125.1	43.91	81.19	1.99

P_2, of ethyl benzoate as a function of the mole fraction N_2. In calculating P_2, it was assumed that the benzene was pure, a necessary assumption if the contamination had been accidental. The dipole moment calculated from the data using impure benzene is 2.40 compared to 2.00 for pure benzene.

Halverstadt and Kumler[4] noted that $P_2 - N_2$ are not linear over the complete range of compositions. Equation 1, if left as a function of N_2, is not linear but does approach a linear relationship at concentrations below $N_2 = 0.1$.

Our value of 1.99 for the dipole moment of ethyl benzoate is in poor agreement with the values, 1.82,[5] 2.14[6] and 2.43,[6] previously reported, and in good agreement with recalculated[4] values of 1.94 and 1.86 for ethyl and methyl benzoate,[6] respectively. Donle's[5] data for ethyl benzoate appear to have a systematic error involved since the value of ϵ_1 was found to be 2.250 instead of 2.282.
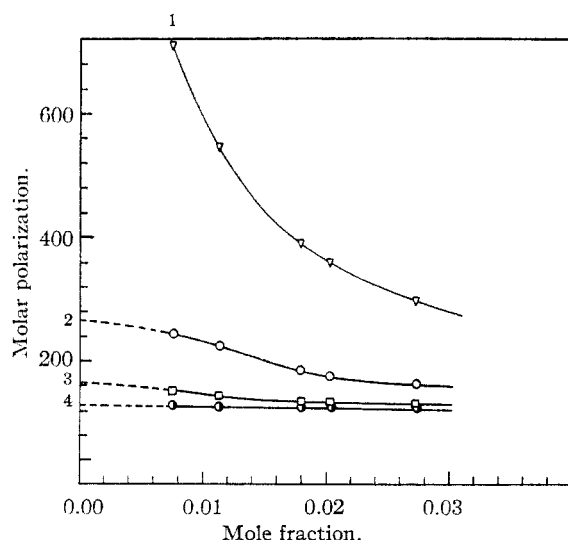

Fig. 3.—Ethyl benzoate: errors in calibration:

	Replaceable capacitance	Vol. of Bob	P_{20}	μ
▲ 1	−40.000	2.6483	>800	>6
○ 2	−48.000	2.6483	>300	>4
◑ 4	−50.628	2.6483	=125	=1.99
□ 3	{−50.000	2.6483	>150	>3
	{−50.628	2.6648	>150	>3

The effect of an error in the value of the replaceable capacitance of the experimental condenser and the volume of the bob used in determining the densities of the solutions was determined by recalculating the values of the dielectric constants and densities of our ethyl benzoate–pure benzene solutions using various assumed values for the replaceable capacitance and volume of bob. The results are given in Fig. 3. If the experimental data fit a smooth curve, a second degree equation can be used. This was proven by checking the data obtained in this Laboratory on phenyl salicylate, and the data on methyl, ethyl and phenyl salicylates.[2] Smith and Cleverdon[7] have also shown the advantage of using a second degree equation to represent the data.

The agreement between the values of P_{20} obtained by the use of equations 1 and 2 is remarkable in view of the magnitude of the errors which were assumed in calculating the above values. The primary factor involved in the use of equations 1 and 2 is internal consistency, and small systematic errors appear to have a negligible effect on the final value of P_{20}. The dipole moments were calculated using the assumption that the sum of the atomic and electronic polarizations was equal to 1.05 R_D, where R_D is the molar refraction. The molar refraction was calculated from the table of atomic refraction.

The results which have been obtained in this work are shown in Table III.

TABLE IV

COMPARISON OF DIPOLE MOMENTS

Compound	μ obsd.	μ rep.
Methyl salicylate	2.53	2.41
Ethyl salicylate	2.69	2.88
Phenyl salicylate	2.27	3.15
Diethoxymethane	0.75	0.92

Discussion of the Dipole Moment Data

The dipole moments obtained for four of the compounds studied in this work are in poor agreement with the previously reported values (Table IV). In view of the similar situation which existed with regard to the moment of ethyl benzoate,[5] the dipole moments of methyl, ethyl and phenyl salicylates[2] and diethoxymethane[8] were recalculated.

(5) H. L. Donle, Z. physik. Chem., **B14**, 326 (1931).

(6) W. J. Svirbely, J. E. Ablard and J. C. Warner, THIS JOURNAL, **57**, 652 (1935).

(7) J. W. Smith and D. Cleverdon, Trans. Faraday Soc., **XLV**, 109 (1949).

(8) M. M. Otto, THIS JOURNAL, **57**, 693 (1935).

The following points were noted concerning the data for the salicylate esters: (1) The concentrations were too high and there are insufficient data in the low range. (2) The data have poor internal consistency.

Although recalculation of the data can at best yield only dubious values of the dipole moments, the following procedure was used: For methyl and ethyl salicylates a second degree equation was fitted to the data over the mole fraction range 0.05 to 0.42. It was assumed that the ϵ_{12} and d_{12} vs. N_2 curves should be linear over the mole fraction range 0 to 0.06 and tangent to the observed curve at mole fraction 0.06. The recalculated value for methyl salicylate is in fair agreement with the value given in Table II, while the agreement in the case of ethyl salicylate is not much improved.

The first six points of the dielectric constant and density data[2] for phenyl salicylate were found to be reasonably linear when plotted against weight fraction. The recalculated value of the dipole moment is 2.41, or 2.37 if only the first three points are considered.

The moment of phenyl salicylate appears to be low when compared with the moments of the other salicylate esters since the moments of phenyl and methyl benzoates (Table V) were 1.87 and 1.88, respectively.

It has been mentioned[9] that the esters of salicylic acid are characterized by internal hydrogen bonding. An examination of the Fisher–Hirschfelder model of phenyl salicylate shows that even with hydrogen bonding, considerable oscillation of the R
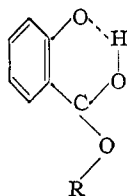
group about the C–O bond of the C–O–R linkage is possible even when R is as large as the phenyl group, provided that the plane of the phenyl group is perpendicular to the plane of the chelate ring. Since the same steric factors exist in the case of phenyl benzoate, the moment of which is very little different from that of methyl benzoate, it seems unlikely that steric hindrance is responsible for the low moment of phenyl salicylate.

Calculation of Dipole Moment from Group

In the case of the methyl o- and p-methoxybenzoates there is no hydrogen bonding to consider. Assuming that the structure of methyl p-methoxybenzoate is equivalent to
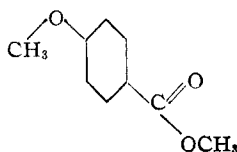
with free rotation of the methoxy group with respect to the ester group, the dipole moment can

(9) G. E. Hilbert, O. R. Wulf, S. B. Hendricks and U. Liddell, THIS JOURNAL, **58**, 548 (1936).

be estimated from the group moments of the methoxy and methyl ester groups. To obtain the group moments the following procedure may be employed.[10] The parallel components of the vectors cancel, and if freedom of rotation is assumed, it is easily shown that the average moment of the rotating perpendicular moments is

$$\mu = \sqrt{2}\mu_1$$

where μ_1 is the value of the vertical component of the methoxy group moment. Taking the value of μ to be the observed moment of the quinol dimethyl ether, 1.7, μ_1 is calculated to be 1.21.

The parallel component of the methoxy group moment, μ_2, is calculated by the vectorial addition of μ_1 and μ_2 to give the observed moment for anisole. That is

$$\mu_2 = \sqrt{1.23^2 - 1.21^2} = 0.22$$

TABLE V
RECALCULATED VALUES

Compound	$P\mu$	μ, recalcd.	μ, report.
Ethyl salicylate	126.7	2.54	2.88
Methyl salicylate	130.3	2.58	2.41
Phenyl salicylate	114.1	2.87	3.15
Ethyl benzoate	85.40	2.03	1.83
Methyl benzoate	73.20	1.88	1.82
Phenyl benzoate	71.90	1.87	1.81
Anisole	31.28	1.23	1.23
	31.28	1.25	1.23
p-Chloroanisole	111.5	2.32	2.24
p-Chloroethylbenzoate	81.00	1.98	2.00
Methyl benzoate	70.79	1.86	2.01
Ethyl benzoate	79.72	1.97	2.14
Hydroquinone dimethyl ether	62.50	1.75	1.81
	59.74	1.71	1.70
Resorcinol dimethyl ether	50.65	1.57	1.59
	51.16	1.58	1.58
Catechol dimethyl ether	20.03	1.08	1.31
	32.46	1.26	1.24
Diethoxymethane	22.11	0.78	0.92
p-Chlorophenol	107.1	2.29	2.68
o-Chlorophenol	36.76	1.34	1.43
Phenol	93.60	2.14	
Chlorobenzene	54.48	1.63	1.52

Similarly, the moment of dimethyl terephthalate, about 2.2, may be represented by two vectors which can be calculated from the moment (1.88) of methyl benzoate (μ_1 1.56, μ_2 1.22).

The moment of p-methyl methoxybenzoate is obtained by the vectorial combination of the vertical and parallel group moments calculated above. The vectors to be combined may be represented by
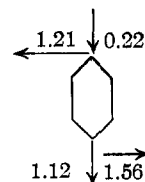
(10) Unless otherwise stated, all quoted values of dipole moments in the following section have been taken from the "Table of Dipole Moments," Trans. Faraday Soc., **30**, 677 (1934). The values were recalculated from the original data, and a comparison of reported and recalculated values is shown in Table V.

The vectors 1.21 and 1.56 are assumed to rotate freely so that the resultant horizontal vector is

$$\mu_r = (1.56^2 + 1.21^2)^{1/2} = 1.97$$

The resultant moment of the compound is then

$$\mu = (1.97^2 + (1.12 + 0.22)^2)^{1/2} = 2.38$$

In view of the uncertainties in the dipole moments used, the calculated value, 2.4, for the moment of methyl p-methoxybenzoate is probably in as good agreement with the measured value, 2.62, as could be expected.

In the case of methyl o-methoxybenzoate the groups are not free to rotate because of steric hindrance. Using the previously obtained values of the group moments and assuming no group interaction the resultant moment of methyl o-methoxybenzoate can be estimated for various positions of the two groups. The results for these calculations may be represented as

(a)   (b)   (c)   (d)   (e)
2.70   2.20   3.13   2.35   2.09
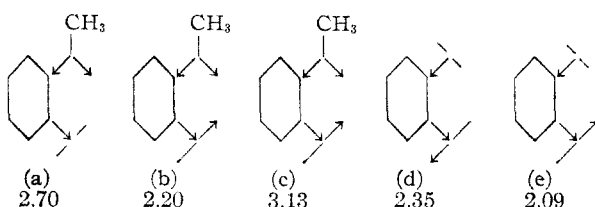
Planes of the methoxy and ester groups are in (a), (d) and (e) perpendicular; in (b) and (c) identical.

The absolute values shown above are probably not too significant but it is interesting to compare them with the value of the moment calculated for methyl p-methoxybenzoate. The calculated increase in moment between the ortho and the para compounds for configuration (a) is of the right order of magnitude, 0.3 compared with the experimentally observed increase 0.22. For the individual forms considered, configuration (a) is the only one which gives a calculated moment increase close to that actually observed. It is necessary to point out, however, that an equimolar mixture of configurations (b) and (c) would result in a measured moment equal to that of configuration (a). The dipole moment data are thus not sufficient to enable one to reach a definite decision with regard to the configuration of the molecule.

An attempt to calculate the moment of the methyl hydroxybenzoates similar to that for the methoxy compounds was not successful. The use of tabulated dipole moment data for various phenol derivatives led to discordant values for the moments μ_1 and μ_2 of the hydroxy group.

It may be noted that in the case of the hydroxy compounds of either methyl or ethyl benzoate the ortho isomer has the lower moment, in contrast to the methoxy derivatives. That this difference

is reasonable may be shown qualitatively in the following way: Let us assume that the moment of the hydroxy group in methyl (or ethyl) p-hydroxybenzoate is approximately perpendicular to the bond joining the oxygen atom to the benzene ring. That the moment vector should be at this angle instead of bisecting the H–O–C bond angle is reasonable in view of the increased positive nature of the oxygen atom due to resonance.

In the case of the ortho compound let us assume that the hydrogen of the hydroxy group is adjacent to the carbonyl oxygen atom of the ester group. If the assumption now be made that the group moments are the same as in the para compound, addition of the vectors indicates that a somewhat lower moment would be expected for the ortho compound. If it is further assumed that because of hydrogen bonding there is a new moment component directed from the hydrogen atom of the hydroxy group to the carbonyl oxygen atom of the ester group, then the addition of this new moment will cause a further decrease in the moment of the ortho compound. The above considerations may be shown diagrammatically as
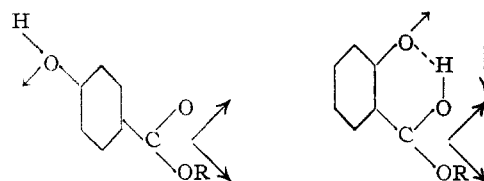
In the case of diethoxymethane,[11] recalculation of the dipole moment from the data reported by Otto[8] gave a value of 0.78, in excellent agreement with the value 0.75 given in Table III. This appears low when compared with the dipole moment of an aliphatic ether of about 1.16, since there are many configurations in which the molecule of diethoxymethane would be expected to be more polar than an ether.

Evidence was obtained for hindered rotation within the molecule, since the molar polarizations of the pure compound, calculated from measurements of the dielectric constants and densities at 25° and 40.7°, are 42.7 and 43.6, respectively. Normally the molar polarization decreases with rising temperature. The observed increase in molar polarization for diethoxymethane is most reasonably interpreted as an increasing freedom of rotation of the C_2H_5–O group about the O–C bond of the O–C–O group.

(11) The investigation of diethoxymethane was undertaken solely as the preliminary step in a projected problem involving a comparison between diethoxymethane and 1,3-dioxine.