

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ELECTRIC MOMENT AND MOLECULAR STRUCTURE. I. THE ETHYL ESTERS OF MONO- AND DICARBOXYLIC ACIDS

By C. P. SMYTH AND W. S. WALLS

RECEIVED DECEMBER 3, 1930

PUBLISHED FEBRUARY 9, 1931

A series of ten papers has been published from this Laboratory under the general title, "The Dielectric Polarization of Liquids,"¹ but, the applicability of the Debye theory to liquids having been definitely established, dielectric investigations can now safely aim more directly at the problems of electric moment and molecular structure, some of which received preliminary treatment in earlier studies.²

Although it was obvious that the complexity of the carboxyl group would complicate the interpretation of the results, the ethyl esters of the dicarboxylic acids appeared to offer a means of investigating the effect upon the resultant electric moment of separating the component moments by a carbon chain of varying length. As this moment is the resultant of the moments of two $-\text{COOC}_2\text{H}_5$ groups, it seemed desirable to give this group more thorough investigation than it had hitherto received by measuring the ethyl esters of formic, acetic and propionic acids.

The dielectric constants of these substances in solution in benzene were measured by means of a heterodyne beat apparatus similar to those employed by several other investigators,³ the wave length used being 1000 meters. As previous work⁴ had shown that the values of large moments obtained from the temperature variation of the polarization did not differ greatly from those calculated from the difference between the polarization at one temperature and the molar refraction, the measurements were carried out at 25° and repeated at 50° as a means of ascertaining the presence of any complicating factors which would vary with temperature. The cell used to contain the liquid to be measured consisted of concentric gold-plated brass cylinders similar to those used in earlier measurements.⁵ An Ostwald-Sprengel pycnometer fitted with carefully ground caps was used for the density measurements. The temperatures were maintained by means of two accurately adjusted thermostats. The refractive indices were measured with a Pulfrich refractometer at 25° for the calculation of the molar refraction and at 20° for comparison with the values contained in the literature, this comparison serving as a means of checking the purity of the materials.

¹ Smyth and co-workers, *THIS JOURNAL*, **50**, 1536, 1547, 1883 (1928); **51**, 1736, 2051, 3312, 3330 (1929); **52**, 1824, 2227, 3546 (1930).

² Smyth and co-workers, *Phil. Mag.*, **45**, 849 (1923); **47**, 530 (1924); *THIS JOURNAL*, **46**, 2151 (1924); **47**, 1894, 2501 (1925); **49**, 1030 (1927).

³ See Williams, *Fortschritte Chem., Physik physik. Chem.*, **20**, No. 5 (1930).

⁴ See Smyth, *THIS JOURNAL*, **51**, 2051 (1929).

⁵ See Smyth and Stoops, *ibid.*, **51**, 3312 (1929).

Preparation of Materials

Benzene was purified as in earlier work.⁶

Ethyl Formate.—Material obtained from the Eastman Kodak Company (b. p. 54–55.5°) was dried with anhydrous sodium sulfate and distilled. The fraction boiling at 54.0–54.5° was redistilled and the fraction at 54.2–54.4° taken for use.

Ethyl Acetate.—Merck's ethyl acetate was shaken twice with concentrated potassium carbonate solution, washed with water, dried with fused potassium carbonate and then with phosphorus pentoxide, and fractionally distilled. The middle fraction was redistilled, b. p. 76.7–76.9°.

Ethyl Propionate.—Material obtained from the Eastman Kodak Company (b. p. 98–100°) was dried with phosphorus pentoxide and distilled. The middle fraction (b. p. 99.05–99.15°) was redistilled and the fraction at 99.10–99.15° taken for use.

Dibasic Acid Esters.—With the exception of the diethyl ester of hexadecamethylenedicarboxylic acid, the materials were obtained from the Eastman Kodak Company. They were dried over anhydrous sodium sulfate or fused potassium carbonate and fractionally distilled under reduced pressure, the middle fraction being taken and redistilled.

Hexadecamethylenedicarboxylic ester was prepared from the acid, which was very kindly loaned to us by Dr. Wallace H. Carothers of E. I. du Pont de Nemours and Company. A solution of the acid in absolute ethyl alcohol was treated with dry hydrogen chloride and, after two hours of refluxing, the excess alcohol was distilled off. After cooling, the product was poured into ice water, treated with sodium carbonate, filtered, washed and dried. It was then recrystallized four times from absolute alcohol and dried in a vacuum desiccator; m. p. 48.3°.

The refractive indices of all the purified liquids are shown in Table I, their good agreement with the values in the literature giving evidence of purity. The molar refraction of the hexadecamethylenedicarboxylic ester given in Table III is calculated from measurements upon the substance in solution. It is only 0.1 higher than the value calculated as the sum of the atomic refractions.

Experimental Results

The data for the pure substances are given in Table I, in which the temperature coefficient of the refractive index for the D sodium line is calculated as the difference between the values at 20 and 25° divided by 5 and the coefficient of the density as the difference between the values at 25 and 50° divided by 25. The indices at 25° and the densities at 50° are omitted for the sake of brevity. In Table II the first column gives the mole fraction c_2 of the ester in the benzene solution and the succeeding columns give the values at 25 and 50° of the dielectric constants ϵ and the densities d of the solutions and the polarizations P_2 of the esters. P_2 is calculated by means of the usual equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{c_1 M_1 + c_2 M_2}{d} \quad \text{and} \quad P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2 , M_1 and M_2 and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual components. For dilute solutions the difference $P_{12} - P_1$ is so small that the error in P_2 may be large, sometimes,

⁶ Smyth and Rogers, THIS JOURNAL, 52, 2227 (1930).

causing single values of P_2 to deviate markedly from a uniform variation with c_2 . In some cases ten or more solutions have been measured in order to fix as accurately as possible the course of the P_2 - c_2 curve, although only enough values are included in Table II to make possible the reproduction of the curve. A number of solutions in heptane also were run as a check on those in benzene, but the few data thus obtained are omitted as they are consistent with the results for the benzene solutions. The extrapolation of the P_2 - c_2 curve to infinite dilution, that is, $c_2 = 0$, gives the value of P_∞ , from which the electric moment μ is calculated by means of the equation

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T}$$

in which MR_D is the molar refraction calculated from the data in Table I, and T is the absolute temperature. In Table III the second column gives the carbon chain which holds the $-\text{COOC}_2\text{H}_5$ group or groups, the third column gives the molar refraction for the D sodium line, and the fourth and

TABLE I
REFRACTIVE INDICES AND DENSITIES OF THE ESTERS

	n_D^{20}	$\Delta n / \Delta t \times 10^5$	d_4^{20}	$\Delta d / \Delta t \times 10^5$
Ethyl formate	1.35987	47	0.9071	130
Ethyl acetate	1.37276	51	.8943	123
Ethyl propionate	1.38414	51	.8842	116
Diethyl maleate	1.44085	54	1.0586	101
Diethyl fumarate	1.44095	54	1.0452	103
Diethyl oxalate	1.41044	45	1.0725	117
Diethyl malonate	1.41411	39	1.0525	107
Diethyl succinate	1.42010	40	1.0349	103
Diethyl glutarate	1.42400	40	1.0170	100
Diethyl adipate	1.42740	40	1.0033	96
Diethyl sebacate	1.43672	38	0.9588	84

TABLE II
DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS OF THE ESTERS

c_2	ϵ	d	P_2
25°	50°	25°	50°
Ethyl Formate			
0.0000	2.276	2.229	0.8734
			0.8468
.0377	2.460	2.387	.8741
			.8472
.0546	2.541	2.457	.8744
			.8475
.1126	2.822	2.708	.8756
			.8484
.1696	3.112	2.960	.8769
			.8494
.2083	3.312	3.137	.8779
			.8502
Ethyl Acetate			
0.0310	2.410	2.341	0.8739
			0.8472
.0475	2.477	2.400	.8742
			.8475
.0614	2.532	2.450	.8744
			.8476
.1060	2.708	2.602	.8752
			.8484
.1575	2.912	2.782	.8762
			.8492

TABLE II (Continued)

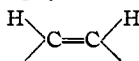
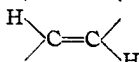
c_2	ϵ		d		P_2	
	25°	50°	25°	50°	25°	50°
Ethyl Propionate						
0.0275	2.388	2.322	0.8736	0.8468	93.2	86.8
.0649	2.534	2.449	.8741	.8471	90.6	85.5
.0900	2.627	2.533	.8744	.8474	88.8	84.8
.1350	2.794	2.684	.8751	.8480	86.7	83.7
Diethyl Maleate						
0.0240	2.481	2.411	0.8813	0.8547	170.5	163.1
.0312	2.542	2.463	.8836	.8571	169.3	161.1
.0574	2.747	2.649	.8919	.8655	162.1	155.9
.0797	2.921	2.807	.8987	.8723	158.3	153.3
.1213	3.216	3.065	.9105	.8841	150.9	146.1
Diethyl Fumarate						
0.0262	2.474	2.405	0.8812	0.8549	157.6	150.9
.0576	2.703	2.611	.8900	.8637	153.3	148.0
.0699	2.793	2.691	.8935	.8672	152.0	146.8
.0878	2.919	2.805	.8984	.8721	149.8	145.1
.1044	3.033	2.907	.9028	.8766	147.8	143.3
Diethyl Oxalate						
0.0318	2.537	2.463	0.8828	0.8561	156.2	150.3
.0492	2.675	2.583	.8879	.8612	152.4	146.0
.0629	2.784	2.680	.8916	.8649	150.2	144.3
.1074	3.104	2.966	.9039	.8771	140.8	136.1
.1381	3.326	3.177	.9121	.8853	136.8	131.2
Diethyl Malonate						
0.0238	2.482	2.412	0.8808	0.8539	167.5	160.8
.0320	2.548	2.470	.8829	.8561	165.1	159.0
.0502	2.706	2.608	.8883	.8615	163.3	156.1
.1087	3.183	3.026	.9045	.8776	153.9	147.9
.1606	3.550	3.362	.9176	.8908	145.1	140.9
Diethyl Succinate						
0.0306	2.457	2.397	0.8829	0.8559	135.3	133.7
.0547	2.596	2.526	.8898	.8630	133.4	132.1
.0729	2.698	2.621	.8949	.8682	132.2	130.8
.0983	2.833	2.748	.9016	.8750	129.8	128.8
.1050	2.871	2.784	.9034	.8768	129.6	128.7
.1531	3.113	3.004	.9153	.8887	126.0	124.8
Diethyl Glutarate						
0.0170	2.405	2.343	0.8782	0.8515	165.5	158.0
.0311	2.510	2.437	.8822	.8555	163.4	157.0
.0544	2.683	2.589	.8886	.8621	161.3	154.7
.0812	2.871	2.762	.8957	.8691	157.7	153.0

TABLE II (Concluded)

c	e		d		P ₂	
	25°	50°	25°	50°	25°	50°
Diethyl Adipate						
0.0165	2.400	2.339	0.8781	0.8513	169.7	163.8
.0250	2.460	2.392	.8805	.8537	167.5	161.2
.0367	2.546	2.469	.8838	.8572	167.0	160.9
.0384	2.558	2.480	.8843	.8577	166.6	160.7
.0779	2.832	2.730	.8945	.8683	162.5	158.1
.0836	2.869	2.763	.8960	.8697	161.7	157.4
Diethyl Sebacate						
0.0119	2.371	2.312	0.8764	0.8496	197.3	189.0
.0182	2.416	2.354	.8779	.8515	193.7	186.7
.0229	2.453	2.383	.8792	.8526	193.9	184.9
.0266	2.480	2.408	.8800	.8536	193.2	185.1
.0273	2.484	2.414	.8802	.8538	192.6	185.8
.0606	2.718	2.619	.8876	.8620	188.7	181.8
Hexadecamethylenedicarboxylic Ester						
0.00000	2.276	2.226	0.8734	0.8465	(26.68	26.76 = P ₁)
.00495	2.315	2.260	.8746	.8479	234.8	224.8
.00967	2.351	2.291	.8753	.8490	235.6	224.3
.01591	2.395	2.331	.8764	.8504	232.9	224.2
.02736	2.476	2.404	.8784	.8528	232.8	224.9
.03125	2.500	2.427	.8790	.8535	231.2	224.6

TABLE III

ELECTRIC MOMENTS OF ESTERS

	Groups on -COOC ₂ H ₅	MR _D	P _∞ - MR _D		25° × 10 ¹⁸	
			25°	50°	25°	50°
Ethyl formate	H—	17.90	78.4	71.5	1.94	1.93
Ethyl acetate	CH ₃ —	22.28	71.7	63.7	1.86	1.82
Ethyl propionate	C ₂ H ₅ —	26.84	68.6	61.1	1.81	1.78
Diethyl maleate		42.68	134.4	125.3	2.54	2.56
Diethyl fumarate		43.26	117.8	110.3	2.38	2.40
Diethyl oxalate	—	33.62	129.4	122.4	2.49	2.52
Diethyl malonate	—CH ₂ —	37.86	134.7	127.1	2.54	2.57
Diethyl succinate	—(CH ₂) ₂ —	42.41	95.4	93.7	2.14	2.21
Diethyl glutarate	—(CH ₂) ₃ —	47.01	120.7	112.5	2.41	2.42
Diethyl adipate	—(CH ₂) ₄ —	52.08	119.9	112.1	2.40	2.42
Diethyl sebacate	—(CH ₂) ₈ —	70.25	128.7	119.9	2.49	2.50
Hexadecamethylene- dicarboxylic ester	—(CH ₂) ₁₆ —	107.0	129.0	117.8	2.49	2.48

fifth columns the differences between this refraction and the values of P_{∞} at 25 and 50°. In the calculation of the moment this difference is treated as the orientation polarization, that is, the polarization due to the orientation of the molecular dipoles. This treatment neglects the small atomic

polarization P_A , which probably increases somewhat with increase in molecular weight, but, in the case of such large polarizations, the error involved in regarding $P_\infty - MR_D$ as the measure of the effect of the dipole is small.⁴ The molar refraction is, of course, the measure of the electronic contribution P_E to the polarization and increases regularly with increase in the size of the molecule. The absolute values of the moments are probably a few hundredths high because of the neglect of P_A , but, relative to one another, they should not be in error by more than $\approx 0.02 \times 10^{-18}$.

Discussion of Results

A few years ago the relative moments of the molecules of mono-carboxylic acids and their esters were calculated⁷ on the assumption of valences acting at the apices of regular tetrahedra with arbitrarily located charges and complete freedom of rotation about the single bonds. The conclusion reached was that the unsubstituted esters and acids should all have the same moment except for the secondary effects of induction and repulsion between groups. A similar type of calculation for the ketones indicated that they should have moments approximately 1.24 times those of the esters. These conclusions were supported by the values of the moments calculated from the dielectric constants by an approximate method, although, as was to be expected, the replacement of an acid hydrogen by an alkyl group altered the moment considerably. Subsequent work showed that this method of calculating the moment from a single value of the dielectric constant could not be relied upon for accurate results because of its failure to correct wholly for the effect of intermolecular action or association. This was evident to some extent at the time of the calculations on the esters, for ethyl acetate gave a value of 1.47×10^{-18} for the moment at room temperature and 1.62×10^{-18} at the boiling point. This latter value is not much lower than those in Table III for ethyl acetate, which are slightly higher than the unpublished value of Zahn for the vapor, 1.76×10^{-18} , and the value 1.74×10^{-18} found by Williams.⁸ It is obvious now, however, that, because of intermolecular action, the small differences in moment calculated in the original investigation were without significance. Recent experimental determinations of the moments of the ketones⁹ show that they are about 1.5 times those of the esters, instead of 1.24, as calculated.

Eucken and Meyer¹⁰ have calculated the moments of molecules by assigning definite moments to chemical bonds. Assuming tetrahedral valences and considering the effect of rotation about the C—O bond in fatty

⁷ Smyth, *THIS JOURNAL*, **47**, 1894 (1925).

⁸ Williams, *Physik. Z.*, **29**, 174 (1928).

⁹ Wolf and Lederle, *ibid.*, **29**, 948 (1928).

¹⁰ Eucken and Meyer, *ibid.*, **30**, 397 (1929).

acids and their esters, they have concluded that there are two extreme positions possible, one giving a minimum moment and the other a maximum. These possibilities are evident in the following formulas, in which the principal moments are shown



For arrangement (a), in which the moments oppose and cancel one another to a considerable extent, Eucken and Meyer calculate a moment 1.1×10^{-18} . (b) is obtained from (a) by a rotation of 180° about the C—O bond. Here the R—O doublet acts in nearly the same direction as the C=O so that the total moment is 3.4×10^{-18} . Intermediate positions about the C—O bond would give intermediate values for the moment. Eucken and Meyer suppose that, in the acids, the tendency of the acid hydrogen to be attracted toward the carbonyl oxygen, the reason for which is evident in the distribution of charges in (a), renders (a) more probable than (b) under ordinary conditions. The moments of the fatty acids should thus be lower than they would be if, in the rotation about the C—O bond, all positions were equally probable. Eucken and Meyer encountered the difficulty that the value found in the literature for the moment of benzoic acid was lower than the minimum value 1.1×10^{-18} calculated for (a). This was also true of values found for several fatty acids.¹¹ The difficulty appears, however, to be removed by the finding of a value of 1.4×10^{-18} for acetic acid together with evidence that the low values found for other acids were in error because of molecular association.¹²

Although such speculation is necessarily uncertain, it is interesting to note that the tendency of an alkyl group to be attracted toward the carbonyl oxygen might be expected to be less than that of an acid hydrogen. This would make structure (a) represent a less probable position for an ester than for an acid so that the former would have a larger moment as shown by the values for the monocarboxylic acid esters in Table III when compared with the value 1.4×10^{-18} for acetic acid. As the energy of rotation about the C—O bond increases with rising temperature, the forces which render one position more probable than another have decreasing influence and a condition is approached in which all positions around the bond are equally probable. This reduction¹³ in the probability of a structure approximating to (a) should result in an increase in moment with temperature, a phenomenon which has been observed by Zahn¹² for the

¹¹ Wolf, *Physik. Z.*, **31**, 227 (1930).

¹² Smyth and Rogers, *THIS JOURNAL*, **52**, 1824 (1930); Zahn, *Phys. Rev.*, **35**, 1047 (1930).

¹³ Meyer, *Z. physik. Chem.*, [B] **8**, 27 (1930).

vapor of acetic acid. If the hypothesis just presented is correct, the esters should show a smaller temperature variation than the acids as their distribution about the C—O bond is a more nearly random one than that of the acids. Actually, Zahn, in measurements as yet unpublished, has found no temperature variation of the moment of ethyl acetate in the vapor state, although a variation might be expected in some region of temperature. The reduction of the mean moment because of the fact that all positions around the C—O bond are not equally probable offers a possible explanation of the high value calculated for the ester as compared to that of the ketone on the assumption of the equal probability of all the positions.

Meyer's calculation of the mutual potential energies of the moments in the —COOH group led to values so high that a temperature of 20,000° would have to be reached for fully excited rotation to occur within the group. If this is correct, the temperature variation which is experimentally possible might well be too small to produce a detectable variation in moment. Zahn attributed the change in the moment of acetic acid vapor which he observed between room temperature and 200° to a transition from one state to a higher state of vibration associated with the —OH group. Meyer calculated 3.5×10^{-18} to be the limiting value of the moment approached at the very high temperatures as the energy of rotation overcomes the mutual attraction of the doublets. This value is actually slightly higher than that calculated by Eucken and Meyer for the structure of maximum moment like that represented by (b). Evidently, attempts at exact calculation of the moments and their temperature changes are exceedingly uncertain, but the hypotheses which have been discussed may be used in a qualitative interpretation of experimental results.

The differences between the moments found at 25 and at 50° for the esters in Table III are no greater than the possible experimental errors except in the case of diethyl succinate. It does not appear significant that the three esters of monocarboxylic acids show a decrease in the values found for the moment from 25 to 50°, while the dicarboxylic acid esters generally show an increase. As it has been shown that any change in the moments of the former esters with rising temperature should be an increase and as Zahn has found no change in the moment of ethyl acetate vapor with temperature, the decrease observed in the moments of the fatty acid esters should be accidental, possibly arising from a small error in the calibration of the cell at the higher temperature. The increase in the moments of the other esters is what would be expected from the increased energy of rotation, but the observed change is too small to be significant without further experimental confirmation except in the case of diethyl succinate.

As the marked drop in moment on passing from the formate to the acetate and the slight drop on passing from the acetate to the propionate

are analogous to the sharp drop in ionization constant on passing from formic to acetic acid and the smaller drop from acetic to propionic acid, it would appear that there is a slight variation in the polarity of the O—R bond with the nature of the group attached to the carboxyl carbon. Naturally, the change from hydrogen to methyl has a greater effect than that from methyl to ethyl. It may be noted that the moment of ethyl benzoate is $1.8 \times 10^{-18,14}$ which shows that the phenyl group has no markedly different effect upon the $-\text{COOC}_2\text{H}_5$. It seems reasonable to assign a value 1.8×10^{-18} to the moment of the $-\text{COOC}_2\text{H}_5$ group when it is attached to a carbon atom, but this moment cannot be treated like that arising from a simple atom or group such as chlorine or nitro because of the effects of the rotation within the group and of the rotation of the group itself. The mean effective moment of the group probably makes an angle with the direction of the bond connecting the group to the rest of the molecule not very different from the tetrahedral angle, but the complexity of the structure arising from rotation and the approximations which would be necessary, render useless an attempt to calculate this angle exactly. If the moment is treated as a fixed moment 1.8×10^{-18} , making the tetrahedral angle 110° with the direction of the bond of the group, the moment resulting from the joining of two groups to form diethyl oxalate may be calculated from the simple equation, $\mu = 1.41 \times 1.8 \times 10^{-18} \sin 70^\circ = 2.4 \times 10^{-18,15}$ in which the effect of the two groups upon each other is disregarded. This value is close to that observed for diethyl oxalate, in which, however, the fields of force of the two groups should so affect one another that some positions in the rotation of the groups about the connecting bond should be much more probable than others. In dimethyl terephthalate, two $-\text{COOCH}_3$ groups, which should have moments close to those of the $-\text{COOC}_2\text{H}_5$, though, perhaps, a little lower, are in para positions on the benzene ring. As the benzene valences lie in the plane of the ring directed out from the center,¹⁶ this means that the two groups are placed relatively to one another just as in the oxalate, except that they are so far separated from one another by the benzene ring that all positions of rotation about the line joining the two carbonyl carbons should be equally probable. The moment found for this molecule,¹⁷ 2.2×10^{-18} , differs from the calculated value by little more than the possible experimental error. The moment 2.5×10^{-18} found by the same investigators for dimethyl *o*-phthalate in which the two $-\text{COOCH}_3$ are attached to the ring in such a way that the group bonds make an angle of 60° with one another instead of pointing in opposite directions shows that the resultant

¹⁴ Estermann, *Z. physik. Chem.*, [B] 1, 422 (1928).

¹⁵ See Williams, *ibid.*, [A] 138, 75 (1928).

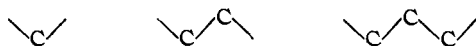
¹⁶ Smyth and Morgan, *THIS JOURNAL*, 49, 1030 (1927).

¹⁷ Estermann, Ref. 14; Weissberger and Williams, *ibid.*, [B] 3, 367 (1929).

moment of the molecule is increased, but only to a small extent, by the introduction of this angle. This is in marked contrast to the behavior of simple groups, for the moment of *p*-dichlorobenzene is zero, while that of *o*-dichlorobenzene is 2.25×10^{-18} .¹⁸

In diethyl fumarate the two $-\text{COOC}_2\text{H}_5$ groups should point in opposite fixed directions and the moment happens to be identical with that calculated for such an arrangement. It must be remembered in considering all of these calculated values that, while, relative to one another, they are significant, absolutely, they can be expected to indicate little more than the order of magnitude. In diethyl maleate the groups make an angle with one another, perhaps acute, and the moment is 0.16×10^{-18} higher than that of the fumarate, the difference resembling qualitatively that between the ortho and para arrangements of similar groups on the benzene ring. That the force fields of the groups affect one another strongly in the *cis* form is shown by the fact that the first ionization constant of maleic acid is ten times that of fumaric, while the second ionization constant of fumaric is about one hundred times that of maleic. The moment of the maleate is probably influenced by the effects of the two groups upon one another, but, in view of the small differences in moment accompanying great differences in the angles between the groups, the effect of the groups upon one another's rotation about the group bonds should not alter the moment greatly. It is evident also that the moment of the molecule as a whole is little affected by possible effects upon the rotation about bonds within the $-\text{COOC}_2\text{H}_5$ groups.

The insertion of the $-\text{CH}_2-$ between the $-\text{COOC}_2\text{H}_5$ groups to form the malonate should introduce the tetrahedral angle between them, that is, set them at an angle of 110° to one another and so raise the moment slightly as observed in Table III. When another $-\text{CH}_2-$ is introduced to form the succinate, the effect is complicated by rotation about the bond between the $-\text{CH}_2-$ groups. However, it is customary to regard a carbon chain as a zig-zag arrangement and Vorländer¹⁹ has found that the tendency to form liquid crystals, which is dependent, to a considerable extent, upon the linearity of the molecules, is greatly reduced by the introduction of a $-\text{CH}_2-$ group into the middle of the molecule of a liquid crystalline substance because of the angle thereby produced in the chain of the molecule. When a second $-\text{CH}_2-$ group is added, the tendency to form liquid crystals is largely restored, while the addition of a third $-\text{CH}_2-$ reduces the tendency once more, etc. The bending of the molecule is obvious if we write the carbon-to-carbon valences in the conventional fashion



¹⁸ Smyth, Morgan and Boyce, *THIS JOURNAL*, **50**, 1536 (1928).

¹⁹ Vorländer, *Z. physik. Chem.*, **105**, 211 (1923).

It would appear that there is a tendency toward such a zig-zag arrangement, but rotation about the bonds in the molecules containing more than one carbon between the $-\text{COOC}_2\text{H}_5$ groups gives the opportunity for all possible arrangements, of which, perhaps, the zig-zag is the most probable. In considering the moments of the molecules containing the $-\text{COOC}_2\text{H}_5$ groups on the ends of these chains, one must bear in mind that not only the orientations of the two groups relative to one another, but also the removal of the two groups from one another's influence by the interposition of carbon atoms may affect the resultant moment of the molecule as a whole.

The rise in moment from the oxalate to the malonate is followed by a drop as expected on going to the succinate, but the magnitude of the drop shown in Table III is much greater than would be expected. When the result was first obtained, the presence of an abnormally large experimental error was suspected, but the purity of the material used was checked satisfactorily and additional measurements agreed with the first. It is possible that the apparent farther removal of the $-\text{COOC}_2\text{H}_5$ groups from one another's influence has some effect, but, if this were the principal cause of the drop, one would expect the moments of the higher members of the series to vary around 2.2×10^{-18} instead of rising again to above 2.4×10^{-18} . Actually, there is reason to believe that, instead of being farther removed from one another, parts, at least, of the $-\text{COOC}_2\text{H}_5$ groups in the succinate may be particularly close to one another, for the anhydride of succinic acid is formed with ease. Dunstan, Hilditch and Thole²⁰ found that the molecular viscosities of these esters gave a smooth curve when plotted against molecular weight except for a sharp hump at the value for the succinate, which lay above those for the malonate and the glutarate. This enhancement of the viscosity was attributed to contiguity of the groups at the ends of the carbon chain. It seems probable then that the structure with two carbons between the $-\text{COOC}_2\text{H}_5$ groups is particularly favorable to those positions of rotation about the bonds in which certain of the doublets are brought close together so as partially to oppose and cancel one another, the mean resultant moment of the molecule being thereby lowered. This idea receives support from the marked rise in moment when the temperature changes from 25 to 50°, for rising temperature, by tending to make all positions equally probable, would increase the moment. It would appear that the succinate is the only one of these esters which may be expected to show much variation of moment with temperature since, in the others, the influences of the $-\text{COOC}_2\text{H}_5$ groups upon one another have little effect upon the resultant moment of the molecule. It may be mentioned that, in examining the optical activity of the menthyl esters and the brucine salts of the fatty dibasic acids, Hilditch²¹ found

²⁰ Dunstan, Hilditch and Thole, *J. Chem. Soc.*, 103, 133 (1913).

²¹ Hilditch, *ibid.*, 95, 1578 (1909).

an exceptionally large temperature coefficient for the rotatory power of dibrucine succinate. The temperature variation of the moments of these substances is being further investigated.

The moment of the glutarate should be approximately the same as that of the malonate if the zig-zag structure of the carbon chain and the consequent angle between the $-\text{COOC}_2\text{H}_5$ groups were maintained, but rotation about the bonds of the chain tends to destroy this arrangement and lower the mean moment. Because of this rotation and flexibility of the chain, the effect of an added carbon atom diminishes with increasing length of the chain. In fact, the fourth carbon added in going from the glutarate to the adipate has no observed effect. If, therefore, the chain does not bend around upon itself with increasing length to form something like a loose ring structure because of the attraction of the $-\text{COOC}_2\text{H}_5$ dipoles for one another, and if it is not so flexible as to bend in the electric field used in the measurement of the dielectric constant and so give partially independent orientation of the two ends of the molecule in the field, the value found for the moment should show little change with increasing length of the chain. The small apparent increase in moment from the adipate to the sebacate might be attributed in part to the neglected P_A of the four added $-\text{CH}_2-$ groups and in part to the effects just mentioned, but the absence of further change when the chain is lengthened by eight more $-\text{CH}_2-$ groups indicates that these effects must be very small. Indeed, if the atomic polarization, P_A , of the eight $-\text{CH}_2-$ groups were equal to that of octane,²² 0.78, it would increase the apparent value of the moment by less than 0.01×10^{-18} . Although it has been shown that the orientation of the $-\text{COOC}_2\text{H}_5$ groups relative to one another does not have a large effect upon the moment of the molecule, the identity of the moment of the very long molecule of the diethyl ester of hexadecamethylenedicarboxylic acid with that of the shorter molecule of the sebacate and the closeness of this value to those for the relatively short molecules would seem to indicate that the long chains do not bend around upon themselves to form ring structures. It would further appear that the extended chains of the long molecules are not so flexible as to bend in the external fields applied in the measurements.

Summary

The dielectric constants and densities of the ethyl esters of a number of mono- and dicarboxylic acids have been measured in benzene solution and have been used, together with the refractions determined for the pure substances, to calculate the electric moments of the molecules. The ethyl esters of the monobasic fatty acids show a slight decrease in moment with increase in the size of the molecule analogous to the decrease in ionization constant.

²² Dornte and Smyth, *THIS JOURNAL*, **52**, 3546 (1930).

Because of rotation around the bonds the relative positions of the $-\text{COOC}_2\text{H}_5$ groups in the molecule do not have large effects upon the moment.

The absence of marked difference in moment between the long and the short-chain esters is regarded as indicating that the long-chain molecules have extended structures, which do not bend appreciably in small external electric fields.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE RAPID COLORIMETRIC ESTIMATION OF POTASSIUM

BY EARLE R. CALEY

RECEIVED DECEMBER 4, 1930

PUBLISHED FEBRUARY 9, 1931

Some months ago the writer published a paper¹ setting forth the merits and demerits of the picric acid test for potassium from a qualitative point of view. Further experiments have since demonstrated that this reaction may be utilized for the colorimetric estimation of small amounts of potassium by separating the precipitated potassium picrate, dissolving it in water, and using the intensely-colored yellow solution thus obtained for the determination of the element.

Factors Influencing the Quantitative Precipitation of Potassium as Picrate by Alcoholic Solutions of Picric Acid.—In addition to the marked influence of the ratio of the volume of the reagent to that of the potassium solution on the sensitivity of the reaction, noted in the previous paper, it was found that the temperature during precipitation was of importance from the quantitative standpoint. In the accompanying graph are shown the results of several experiments (Fig. 1) in which the amount of potassium picrate precipitated at various room temperatures is compared colorimetrically with that precipitated at 20°. This effect is apparently due to the rapid increase in the solubility of the precipitate with rise in temperature. It is evident that for comparative quantitative results in any colorimetric method involving this reaction the potassium, in a single series of experiments where standards and samples are prepared for matching, they must be precipitated under like temperature conditions or, better, a definite temperature must be established for all precipitations. It is apparent from the graph that for the sake of greater completeness of precipitation this temperature should be nearer the lower limits of room temperature rather than the higher. A temperature of 20° was found to be satisfactory. Temperatures much below this, while resulting in the more complete precipitation of the potassium, are not satisfactory due to the precipitation of the picric acid from the reagent saturated at room temperature and to

¹ Caley, *THIS JOURNAL*, 52, 953 (1930).