371. *The Dipole Moments of Some Long-chain Molecules.*

By John W. Smith.

It has generally been assumed that the electrical dipoles of straight-chain molecules, such as those of fatty acids, are located almost entirely in the heads of the molecules, and that inductive effects do not extend along the chain beyond the first two or three carbon atoms. This view has been supported by the observation that, *e.g.*, although the dipole moment of ethyl alcohol differs somewhat from that of methyl alcohol, it has very nearly the same value as that of propyl alcohol; and in general, the values of the dipole moments in any homologous series tend to become constant after the second member.

The electric moments of a few homologous series of compounds are collected in Table I. The values given are approximately the mean of data obtained by different experimenters, except that, in the same series, preference is given to results from the same source, in order to render the values more closely comparable.

TABLE I.

Dipole Moments (× 10^{18}) *of Homologous Series of Straight-chain Aliphatic Compounds.*

	Cl.	Br.	I.	OH.	NH_2.	CHO.	CN.
(H)	1·03	0·79	0·38	1·85	1·5	—	2·65
CH_3	1·85	1·5	1·3	1·68	1·23	2·7	3·11
C_2H_5	1·99	1·83	1·66	1·70	1·3	—	3·34
C_3H_7	2·0	1·8	1·6	1·66	1·4	2·46	3·46
C_4H_9	1·97	1·97	1·88	1·65	1·3	—	—
C_5H_{11}	—	—	—	—	1·3	—	—
C_6H_{13}	—	—	—	1·6	—	2·56	—
C_7H_{15}	1·85	1·84	1·84	1·71	—	—	—

The measurements which have been recorded are generally confined, however, to the first four or five members of a series, and no actual measurements appear to have been made of the electric moments of any long-chain molecules, apart from those of Mahanti and Das Gupta (*Indian J. Physics*, 1929, **3**, 467), who found that the value 1·6—1·7 × 10^{-18} remained fairly constant for primary alcohols up to *n*-dodecyl alcohol.

In view of the possible experimental errors in dipole moment measurements, and especially as many of the earlier determinations in this field were rather inaccurate, investigations with higher members of one or two other series appeared to be desirable in order to make certain that the moment really remains constant, and that it does not change slowly but progressively with the length of the chain; to this end, those of myristic acid, palmitic acid, and methyl myristate have now been determined.

The long-chain fatty acids are of particular interest in view of the discordant results which have been obtained for the dipole moments of the lower members of the series, doubtless owing to their tendencies to associate in some solvents, solvate in some, and to ionise in others. This point will be discussed later (p. 1569).

EXPERIMENTAL.

Materials.—The purest obtainable benzene was dried over sodium wire, recrystallised twice, dried again, fractionally distilled from phosphoric oxide, and then treated with successive quantities of sodium wire until the latter retained completely its metallic lustre. It was quite free from thiophen.

Palmitic and myristic acids and methyl myristate were presented to the author in the pure state, and were used as received.

Measurement of the Electrical Dipole Moments.—The dielectric constants of dilute solutions of the compounds in benzene were measured by the method already described by the author (*Proc. Roy. Soc.*, 1932, *A*, **136**, 251). The measurements were made in each case at 25·0° ± 0·1°, and the densities of the same solutions were measured at the same temperature with an accurate form of pyknometer. The molecular polarisations of the solutes were calculated from these results by application of the well-known modification of the Clausius–Mosotti equation.

The electronic polarisations are assumed to be identical with the molecular refractivities as calculated from the sum of the group refractions (Smyth, " Dielectric Constant and Molecular Structure," New York, 1931, p. 151); calculation from the refractive indices of the solutions was not desirable, because these differed only very slightly from the value for pure benzene.

The concentration range over which the measurements could be carried out was limited by the relatively sparing solubility of the compounds, especially palmitic acid, in benzene.

The experimental results are in Table II, where the symbols have their usual significance. The value 2·2725 for the dielectric constant of benzene at 25° is taken as standard.

Palmitic acid: $P_{1\infty} = 99{\cdot}2$; P_E (calc.) $= 76{\cdot}4$; hence $P_A + P_O = 22{\cdot}8$ c.c.

Myristic acid: $P_{1\infty} = 89{\cdot}0$; P_E (calc.) $= 67{\cdot}2$; hence $P_A + P_O = 21{\cdot}8$ c.c.

Methyl myristate: $P_{1\infty} = 135{\cdot}1$; P_E (calc.) $= 71{\cdot}9$; hence $P_A + P_O = 63{\cdot}2$ c.c.

If we were able to ignore the atomic polarisation, these figures would lead directly to values of 1·05, 1·02, and 1·74 × 10^{-18} e.s.u. respectively for the dipole moments. However, owing to the fact that in each case $P_A + P_O$ is relatively small compared with P_E, it is most probable that the contribution of P_A to this figure is not inconsiderable. Consequently neglect of P_A

TABLE II.

f_1.	$M_1f_1 + M_2f_2$.	ϵ.	ρ.	$P_1f_1 + P_2f_2$.	P_2f_2.	P_1f_1.	P_1.
0	78	2·2725	0·8738	26·585	26·585	—	—
Palmitic acid.							
0·002012	78·358	2·274	0·8738	26·731	26·532	0·199	98·9
0·005052	78·899	2·276	0·8737	26·951	26·451	0·500	98·4
Myristic acid.							
0·009024	79·354	2·278	0·8736	27·136	26·345	0·791	87·7
0·01837	80·756	2·282	0·8733	27·685	26·097	1·588	86·4
Methyl myristate.							
0·01037	79·701	2·308	0·8733	27·710	26·309	1·401	135·1
0·02332	81·824	2·350	0·8726	29·101	25·965	3·136	134·5
0·04913	86·057	2·429	0·8713	31·867	25·279	6·588	134·1

would introduce a considerable error; and it is better to assume, with Wolf (*Physikal. Z.*, 1930, **31**, 227), that the atomic polarisation is about 15% of the electronic polarisation. Then we have for palmitic acid : P_0 = 11·2 c.c., μ = 0·72 × 10^{-18} e.s.u.; myristic acid : P_0 = 11·7 c.c., μ = 0·76 × 10^{-18} e.s.u.; methyl myristate : P_0 = 53·5 c.c., μ = 1·61 × 10^{-18} e.s.u.

DISCUSSION OF RESULTS.

In Table III the result obtained for methyl myristate is compared with measurements reported for other esters of the fatty acids. Since, with the exception of one series of results, very few data are recorded for the dipole moments of methyl esters, the values obtained for some ethyl esters are also added, together with those for methyl and ethyl benzoates.

TABLE III.

Dipole Moments of Esters (× 10^{18}).

Methyl acetate	1·67[1]; 1·75[3]; 1·74[6]	Ethyl propionate	1·81[3]; 1·74[6]
Methyl propionate	1·69[6]	Ethyl butyrate	1·74[6]
Methyl butyrate	1·71[6]	(Methyl benzoate	1·86[5])
Methyl valerate	1·61[6]	(Ethyl benzoate	1·8[5])
Ethyl formate	1·94[2]	Methyl myristate	1·61
Ethyl acetate	1·74[1]; 1·81[3, 4, 6]; 1·86[2]		

[1] Krchma and Williams, *J. Amer. Chem. Soc.*, 1927, **49**, 2408; [2] Smyth and Walls, *ibid.*, 1931, **53**, 527; [3] Müller and Sack, *Physikal. Z.*, 1930, **31**, 815; [4] Smyth and Dornte, *J. Amer. Chem. Soc.*, 1931, **53**, 2005; [5] Estermann, *Z. physikal. Chem.*, 1928, *B*, **1**, 422; [6] Wolf and Gross, *ibid.*, 1931, *B*, **14**, 305.

From these data it is apparent that the electric moment of methyl myristate falls well into line with the values obtained by Wolf and Gross for the lower methyl esters, the same approximation being used with respect to the atomic polarisation. Even if this polarisation be neglected, the value obtained does not diverge very appreciably from these figures. The most probable value, however, is a little lower than that for methyl acetate and considerably below that for methyl benzoate. This tends to confirm the usual assumption that the length of the carbon chain has scarcely any influence on the dipole moment of a molecule beyond the first two or three members, and that the electric doublet is located almost completely in the head of the molecule.

Analysis of the results for the long-chain acids is not such a simple matter, however. The results deduced for the dipole moments of the lower fatty acids by various authors are very discordant, principally owing to differences in interpretation of the association effects in different solvents. There have been four main series of results on these compounds, and these are summarised in cols. 1—4 of Table IV. They are as follows :

(1) Wolf's measurements (*Physikal. Z.*, 1930, **31**, 227) for benzene solutions, the dipole moments being calculated for the monomeric compounds, the association of the fatty acid molecules in this solvent being ignored, and the atomic polarisation assumed to be 15% of the electronic polarisation. Hence his values are really r.m.s. values for all individual acetic acid, etc., molecules present in solution irrespective of their states of association.

(2) Smyth and Rogers's values (*J. Amer. Chem. Soc.*, 1930, **52**, 1824), calculated for the monomeric forms from results obtained with ethereal solutions. Their deductions are based on the assumption that the dipole moments of the dimeric forms (encountered in benzene solutions) are almost zero, the difference between the total polarisation and the molecular refraction in benzene solution being attributed to atomic polarisation.

TABLE IV.

Dipole Moments of Fatty Acids (× 10^{18}).

Acid.	1.	2.	3.	4.	Acid.	1.	2.	3.	4.
Formic	1·19	—	1·51	1·45	*n*-Butyric	0·68	—	—	0·93
Acetic	0·74	1·4	1·73	1·04	*iso*Valeric	0·63	—	—	0·89
Propionic	0·63	—	1·74	0·88					

(3) Zahn's measurements (*Physical Rev.*, 1931, **37**, 1516) for the monomeric forms of the acids, from the dielectric constants of the gases at high temperatures and low pressures, conditions such that only the single molecules can exist. Zahn also calculated a value of 0·99 for the double molecule of formic acid.

(4) Brieglieb's figures (*Z. physikal. Chem.*, 1930, *B*, **10**, 205), calculated for the dimeric forms. His results, obtained with benzene solutions, show wide experimental discrepancies from those of Smyth and Rogers, and his interpretation of the results is totally different. However, these figures may be taken as definite upper limits to the dipole moments of the dimeric forms.

Comparing these data with the values for palmitic acid and myristic acid calculated above, it is evident that the latter lie appreciably above the values calculated in a similar manner by Wolf for propionic, *n*-butyric, and *iso*valeric acids, and are closer to the figure obtained by him for acetic acid. In view of the result obtained with methyl myristate, however, it would be anticipated that these acids, in the same state of association, would possess dipole moments sensibly equal to those of butyric and valeric acids. The present results, therefore, confirm the general conception that the degree of association of fatty acids in benzene solution decreases with increase in the molecular weight of the acid. On the other hand, the figures lie far below the values obtained by Zahn for the monomeric forms of acetic and propionic acids, the only reliable basic results in this field. Therefore it may be further concluded that there is still considerable association in benzene solution, even for these high members. The relationships between these results become even more pronounced if, as suggested by Smyth and Rogers, the atomic polarisation exceeds 15% of the electron polarisation. This would reduce Wolf's values still lower, whereas, since most of the atomic polarisation is probably located in the chemically polar carboxyl group, the 15% deduced is probably ample for the higher acids.

SUMMARY.

From measurements of the dielectric constants and densities of dilute solutions of palmitic acid, myristic acid, and methyl myristate in benzene, and assuming that the atomic polarisation of these molecules is approximately 15% of the electronic polarisation, their electrical dipole moments (× 10^{18}) have been evaluated as 0·72, 0·76, and 1·61, respectively. These results are discussed with reference to the variation of the electric moment of a molecule with the length of the carbon chain, and also with reference to the association of fatty-acid molecules in benzene solution.

My thanks are due to Dr. N. K. Adam for his gift of the pure compounds, and to Professor F. G. Donnan for his interest in these investigations.

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[*Received, August* 21*st*, 1933.]