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AN INVESTIGATION OF A SERIES OF DERIVATIVES OF NORMAL HEPTANE. II. DIPOLE MOMENTS AND MOLECULAR CONSTITUTION[1]

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The dipole moments of various aliphatic compounds containing one or more polar groups have been determined,[2] but it seemed advisable to study the effect on the moment of the position of the polar group in an aliphatic compound.

In order to have several different positions available a study of a series of derivatives of the straight chain heptane was begun, for in normal heptane it is possible to have a single substituent in four different positions in the molecule. The dipole moments of the four alcohols, heptanol-1 (*n*-heptyl alcohol), heptanol-2 (methyl-*n*-amyl carbinol), heptanol-3 (ethyl-*n*-butyl carbinol), heptanol-4 (dipropyl carbinol) have been measured. The three ketones, 2-heptanone (methyl-*n*-amyl ketone), 3-heptanone (ethyl-*n*-butyl ketone) and 4-heptanone (dipropyl ketone) have been prepared and purified and the moments of these and of the *n*-heptaldehyde have been determined. The chloro and the bromo derivatives corresponding to each of the heptanols have been synthesized and two of the iodo derivatives, 1-iodoheptane and 3-iodoheptane, have also been studied. Great care was taken in the preparation of these compounds to avoid any shift of position in the chain. The preparation of these derivatives and the proof of the position of the groups has been given by one of the authors.[3] The dipole moment of each of the compounds has been calculated from measurements of the dielectric constants of dilute solutions of the compound in a non-polar solvent, benzene, according to the well-known method

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[1] A preliminary report of this work was made at a Symposium in Leipzig, June, 1929, and has been published, p. 41, in "Dipolmomente und Chemische Struktur," herausgegeben von Professor P. Debye, Verlag von S. Hirzel, Leipzig, **1929**. See also Ref. 1, preceding article, M. L. Sherrill, THIS JOURNAL, **52**, 1982 (1930).

[2] (a) Debye, "Polare Molekeln," pp. 39, 45, 52, 59, etc., p. 191 (complete tables), Leipzig, **1929**, "Polar Molecules," New York, **1929** (less complete data); (b) Errera, *J. phys.*, [6] **6**, 390 (1925); *Compt. rend.*, **182**, 1623 (1926); *Physik. Z.*, **27**, 764 (1926); **29**, 689 (1928); "Polarization Dielectrique," Presses Universitaires, Paris, **1928**; (c) Ghosh, *Nature*, **123**, 413 (1929); *C. A.*, **23**, 3383 (1929); (d) Gross, *Physik. Z.*, **30**, 504 (1929); (e) Höjendahl, "Dissertation," Kopenhagen, **1928** (tables and bibliography); (f) Lange, *Z. Physik*, **33**, 169 (1925); (g) Sänger, *Physik. Z.*, **27**, 556 (1926); (h) Smyth, THIS JOURNAL, **46**, 2151 (1924); **51**, 2380 (1929); (i) Smyth and Morgan, *ibid.*, **50**, 1547 (1928); (j) Smyth and Stoops, *ibid.*, **51**, 3312 (1929); (k) Williams, *Physik. Z.*, **29**, 174 (1928); *Z. physik. Chem.*, **138A**, 75 (1928); (l) Wolf, *ibid.*, **2B**, 39 (1929).

[3] M. L. Sherrill, THIS JOURNAL, **52**, 1982 (1930).

shown by Debye.[4] The resonance method was used and the wave length was 100 meters. The capacity measurements were of a precision of 1 part in 500.

The total polarization of a pure substance is regarded as made up of three parts, the polarization P_E caused by electronic shifts induced in the molecule, the polarization P_A attributed to atomic shifts and P_P, the polarization due to orientation of the permanent dipoles in the molecule.[5] The total polarization is determined according to the equation $P = \epsilon - 1/\epsilon + 2 \cdot M/d$, in which ϵ is the dielectric constant, M is the molecular weight and d is the density of the compound. P_∞ is the total polarization of the unassociated molecule obtained by extrapolation of $P_{1,2}$ and P_2 from the data of the dilute benzene solutions, in which $P_{1,2} = \epsilon - 1/\epsilon + 2 \cdot C_1M_1 + C_2M_2/d$ and $P_2 = P_{1,2} - C_1P_1/C_2$. Since it was not possible, at this time, to measure the refractive indices in the long waved infra-red, instead of measuring $P_E + P_A$, P_E was determined from the refractive index of the compounds obtained by measuring the helium yellow line at 20°. P_E is considered equal to the molecular refractivity RM as defined by the Lorenz-Lorentz law, $P_E = n^2 - 1/n^2 + 2 \cdot M/d$, in which n is the refractive index, M the molecular weight and d the density. The dipole moment μ is calculated according to Debye,[6] $\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - P_E)T}$.

According to one of the authors,[7] the molecular association in a liquid may be considered as the result of two factors. The first is the dipolar molecular association which may be attributed to the electrostatic forces of the permanent dipoles in the molecule, these forces being determined by the size and position of the dipoles in the molecule and the form of the molecule itself. The second is the molecular association of the molecules which are not dipoles, which may be the result of intermolecular attraction as indicated by van der Waals. The total association, the sum of these two factors, must be determined by measurements such as vapor pressure, viscosity and surface tension. Polarization measurements, which give the electric moment in unit volume, are able only to give some insight into the first factor of this association corresponding to the association of the dipoles. In fact, in the consideration of the total polarization, $P = P_E + P_A + P_P$, Debye has shown that $P_E + P_A$ corresponds to the polari-

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[4] P. Debye, *Handbuch der Radiologie*, **6**, 597 (1925); "Polare Molekeln," Leipzig, **1929**, p. 46; "Polar Molecules," New York, **1929**, p. 44.

[5] J. Errera, "Polarization Dielectrique," Les Presses Universitaire de France, **1928**.

[6] P. Debye, "Polare Molekeln," Leipzig, **1929**, p. 51; "Polar Molecules," New York, **1929**, p. 49.

[7] J. Errera, *Z. physik. Chem.*, **138A**, 332 (1928); **140A**, 273 (1929); "Dipolmomente und Chemische Struktur," herausgegeben von P. Debye, Leipzig, **1929**, p. 105; "L'Activation et la Structure des Molecules," Réunion Internationale de Chimie-Physique, Paris, **1928**, p. 236.

zation of those constituents whose field is determined by the van der Waals molecular attraction. For a substance whose molecules are not dipoles and whose total polarization is limited to $P_E + P_A$ it is not possible to determine the association through polarization measurements. Where, however, there are dipole molecules present, the association of the permanent dipoles affects greatly the P_P factor. It is then possible to determine the dipolar association, y, of the permanent dipoles present by the ratio of the total polarization at infinite dilution of the permanent dipoles, P_{P_∞} $(P_{P_\infty} = P_\infty - P_E)$, to the total polarization of the permanent dipoles in pure state, P_P $(P_P = P - P_E)$, or $P_{P_\infty}/P_P = y$. In the data for the various series of compounds tabulated below, P_E is a first approximation in place of $P_E + P_A$. The probable error in the dielectric measurements is 0.5%.

TABLE I

CONSTANTS OF HEPTANE DERIVATIVES AT 22°

Derivative	d_4	ϵ	P	P_∞	P_E	$\mu \times 10^{18}$	y
Heptanol-1	0.8214	12.10	110.90	98.0	36.08	1.71	0.83
Heptanol-2	.8153	9.21	104.30	97.5	36.07	1.71	.90
Heptanol-3	.8194	6.86	93.69	97.5	35.98	1.71	1.07
Heptanol-4	.8170	6.17	89.97	97.0	35.96	1.70	1.13
Heptaldehyde	.8206	9.07	101.40	172.8	34.64	2.56	2.06
Heptanone-2	.8006	9.77	106.20	176.0	35.21	2.59	1.98
Heptanone-3	.8167	12.88	111.60	197.0	34.49	2.78	2.11
Heptanone-4	.8160	12.43	110.80	190.0	34.39	2.72	2.04
1-Chloroheptane	.8702	5.48	92.65	111.4	39.50	1.85	1.34
2-Chloroheptane	.8651	6.52	100.60	126.3	39.50	2.03	1.42
3-Chloroheptane	.8674	6.70	101.40	127.0	39.47	2.04	1.41
4-Chloroheptane	.8694	6.54	100.20	127.2	39.40	2.04	1.44
1-Bromoheptane	1.1342	5.38	93.71	113.2	42.39	1.85	1.40
2-Bromoheptane	1.1255	6.46	102.70	131.8	42.50	2.06	1.48
3-Bromoheptane	1.1341	6.93	104.80	130.0	42.42	2.04	1.40
4-Bromoheptane	1.1330	6.81	104.10	130.3	42.40	2.04	1.42
1-Iodoheptane	1.3736	4.90	93.03	117.0	47.60	1.84	1.53
3-Iodoheptane	1.3656	6.39	106.40	126.3	47.99	1.93	1.34

The results show that in the case of the hydroxy group in straight-chain hydrocarbons, such as the heptanols, the dipole moment is independent of the position of the polar group in the chain. It is also to be noted that the association is greatest in the case of 4-heptanol and decreases in order to 1-heptanol, which is least associated, for the dipole moment of each of the four alcohols is the same and the density practically the same, yet the dielectric constant which should be the same varies from $\epsilon = 6.2$ in 4-heptanol to $\epsilon = 12.1$ in the case of 1-heptanol. In the carbonyl derivatives, one of which is an aldehyde, the other three being ketones, it is found that the dipole moment of the 1-derivative, *n*-heptaldehyde, is smaller than that of the 3- and 4-heptanones. The 2-heptanone instead of being like the 3- and 4-derivatives has a dipole moment more like that of *n*-heptaldehyde. This seems to correspond somewhat to the chemical reactivity, for of these compounds only the aldehyde and the 2-heptanone form bisulfite addition products. The dipole moments of a number of ketones have been determined by Wolf,[8] and dipropyl ketone is one of these for which he found a value of $\mu \times 10^{18}$ of 2.73, which checks the value obtained in this work.

In the case of the halogen derivatives it is seen that in the 2-, 3- and 4-positions the dipole moment is practically independent of the position in the chain. In 1-chloro-, 1-bromo- and 1-iodoheptane the dipole moment is smaller than that of the other halogen derivatives. The dipole moment of *n*-heptylbromide is given by Smyth[9] as 1.86, which compares favorably with the value found in this work. From the data obtained with these halogen compounds of heptane it is to be inferred that the dipole moment is the same for the chloro, bromo and iodo derivatives of the aliphatic compounds as Williams[10] has found for the chloro and bromo derivatives of aromatic compounds, the numerical value, however, being greater than for the aromatic derivatives. For the disubstituted chlorides and bromides of benzene and of ethylene one of the authors[11] has found that the moment of the chloro derivatives was larger than that of the bromo and of the bromo larger than the iodo derivatives. In these heptane derivatives the dipole moment of the halogen compounds has been found to be greater than that of the hydroxyl derivative, which is different from that found for aromatic compounds,[10] where the dipole moment of the hydroxy derivative is greater than that of the halogen derivative. The characteristic moment of the polar substituents in *n*-heptane are tabulated below. The values are approximate in the sense that P_A, which in certain cases has a value which cannot be neglected, has not been taken into consideration.

TABLE II

CHARACTERISTIC MOMENTS ($\mu \times 10^{18}$) OF POLAR SUBSTITUENTS IN *n*-HEPTANE

Group	OH	H—C=O	C=O	Cl	Br	I
First position	1.70	2.55	(2.58) (2-ketone)	1.85	1.85	1.80
Other position	1.70	..	2.75	2.00	2.00	1.90

In addition to the alcohol derivatives of heptane there were available three of the petanols (*n*-amyl alcohol,[12] methyl propyl carbinol and diethyl carbinol). The dielectric constants of these alcohols were measured and the dipole moments calculated as in the case of the heptane derivatives.

Here as in the heptanols it is evident that the moment is independent of

[8] K. L. Wolf, *Zeit. physik. Chem.*, **2B**, 39 (1929).

[9] C. P. Smyth, THIS JOURNAL, **51**, 2385 (1929).

[10] J. W. Williams, *ibid.*, **50**, 2350 (1928).

[11] J. Errera, *J. phys.*, **6**, 390 (1925).

[12] Obtained from Professor Timmermans, University of Brussels.

TABLE III

PENTANE DERIVATIVES AT 22°

Derivative	d_4	ϵ	P	P_∞	P_E	$\mu \times 10^{18}$	y
Pentanol-1	0.8134	14.37	88.53	84.0	26.80	1.65	0.93
Pentanol-2	.8100	13.82	88.43	85.0	26.88	1.66	.94
Pentanol-3	.8142	13.02	86.82	83.0	26.52	1.64	.94

the position of the substituent in the molecule; the numerical value of the moment, 1.65, is, however, slightly smaller than that obtained for the heptanols, 1.70. Representative data on electric moments of the straight-chain alcohols as given in the literature are as follows: methyl alcohol, 1.73 (gas),[2e] 1.64 (solution);[13] ethyl alcohol, 1.63,[10] 1.72,[2e] 1.64;[14] *n*-propyl alcohol 1.66,[14] 1.53;[2f] *n*-butyl alcohol 1.65,[2f] 1.75;[2j] octyl alcohol 1.71.[2j] A comparison of these values with the electric moments of the C_5 and C_7 alcohols obtained in this study shows fairly good agreement.

Summary

Dielectric constant data have been obtained for the following compounds, pure and in benzene solution: four straight-chain heptanols, the *n*-heptaldehyde, the three ketones, the four chloro and four bromo derivatives and 1-iodo and 3-iodoheptane. From these data the electric moments have been determined.

The position of the polar group in the chain in the case of the alcohols has been found to have no effect. In the case of the halogen derivatives, the moment is found to be the same for chloro, bromo and iodo compounds but a slightly smaller moment is obtained when the substituent is in the 1-position than when it is in either of the other positions.

The electric moment characteristic of each of the groups, hydroxyl carbonyl and halogen, as shown in aliphatic compounds has been tabulated.

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[13] Stranathan, *Phys. Rev.*, **31**, 653 (1928).

[14] Debye, *Handbuch der Radiologie*, **6**, 390 (1925).