

DIPOLE MOMENTS OF SATURATED DICARBOXYLIC ACIDS

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ABSTRACT

The dipole moments of oxalic, malonic, succinic, glutaric and adipic acids in dioxan have been reported and discussed in relation to their molecular structure. It is shown that the carboxyl groups of these acids exhibit rotation in dilute solutions of dioxan. The dissociation constants of these acids have also been discussed in relation to their dipole moments.

1. INTRODUCTION

In this paper the dipole moments of anhydrous oxalic acid, malonic acid, succinic acid, glutaric acid and adipic acid in dioxan are reported. Dipole moment data for these saturated dicarboxylic acids are not available in the literature except in the case of adipic acid, the moment of which was reported as 4.04 D (in dioxan) by Tseng, Sun and Yao (1937). The moment value for the diethyl adipate being only 2.40 D (Smyth and Walls, 1931), it was felt that a redetermination of the moment of this acid was essential. The comparative insolubility of these acids in usual non-polar solvents has been the main obstacle in the study of their dipole moments. However, they are sufficiently soluble in dioxan so as to enable a determination of their dipole moments. The interest in the moment values of these acids arises also from the point of view of the structure of the carboxyl group, the relative disposition of the two carboxyl groups and their mutual interaction as well. The lengthening of the chain as we proceed from malonic acid onwards might reduce the mutual interaction between the two carboxyl groups and give them rotational freedom. We may therefore expect some evidence for this from the dipole moment studies. Further, from dipole moment measurements on monocarboxylic acids in dioxan it has been pointed out by Wilson and Wenzke (1934) that as a solvent dioxan is able to break up hydrogen bonds between the acid molecules. The results thus obtained in dioxan will therefore be of much significance in the study of the molecular structure of these acids particularly with reference to internal rotation of the carboxyl group.

2. EXPERIMENTAL

1:4 Dioxan (Eastman Kodak) was purified using the method suggested by Eigenberger (1931). The purified product was fractionally distilled over sodium. Boiling point = 101.5°C. (Corr.); $d_{35}^{20} = 1.01694$; $n_D^{35} = 1.41532$.

Anhydrous oxalic acid was prepared from pure oxalic acid dihydrate crystals by distillation with pure toluene according to the method given by Johnson and

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Partington (1930). All the other acids were purified by several recrystallizations from absolute ethyl alcohol.

The apparatus used for the measurement of dielectric constants has been already described by the author in an earlier publication (Narasimhan, 1953). A constant voltage transformer was used to supply the A.C. voltage for the measuring unit. The dielectric cell used was of the Sayce-Briscoe type.

Densities were measured by means of an Ostwald-Sprengel pycnometer. Refractive indices were measured with a Pulfrich refractometer using a divided cell provided with a jacket for water circulation from a thermostat.

3. RESULTS

The mathematical extrapolation method of Hedestrand (1929) was employed for the computation of dipole moments from the dielectric constant and density data of dilute solutions. Atomic polarization was taken as 5% of the molar refraction (MR_D). Results obtained are entered in Tables I to IX. All the measurements were made at a temperature of 35°C.

TABLE I
Anhydrous Oxalic Acid in Dioxan

No.	Mole fraction $f_1 \times 10^6$	Dielectric Constant ϵ	Density d	$\alpha\epsilon_2$	β
1	0	2.1922	1.01694
2	3,095	2.2300	1.01808	12.213	0.362
3	4,524	2.2477	1.01870	12.268	0.383
4	7,135	2.2788	1.01973	12.137	0.385
5	7,787	2.2859	1.02011	12.033	0.400

Total Polarization $T^P_\infty = 195.81$ c.c. $1.05 MR_D = 15.23$ c.c. (calcd.).

Orientation Polarization ${}_0P = 180.58$ c.c. $\mu = 3.00$ D.

TABLE II
Malonic Acid in Dioxan

No.	$f_1 \times 10^6$	ϵ	d	$\alpha\epsilon_2$	β
1	0	2.1922	1.01694
2	6,457	2.2566	1.01948	9.974	0.387
3	14,390	2.3284	1.02258	9.465	0.385
4	22,256	2.4028	1.02586	9.463	0.394
5	32,686	2.5017	1.02962	9.469	0.381

$T^P_\infty = 159.83$ c.c. $1.05 MR_D = 20.12$ c.c. (see Table III).

${}_0P = 139.71$ c.c. $\mu = 2.64$ D.

TABLE III

Molar Refraction of Malonic Acid in Diozan (Na D)

$M_1f_1 + M_2f_2$	88.06	88.16331	88.29024	88.41610	88.58298
f_2	1	0.99354	0.98561	0.97774	0.96731
n_{12}	1.41532	1.41557	1.41594	1.41626	1.41666
n_{12}^2	2.00313	2.00384	2.00489	2.00579	2.00693
d	1.01694	1.01948	1.02258	1.02586	1.02962
$R_1f_1 + R_2f_2$	21.699	21.682	21.664	21.640	21.620
R_2f_2	21.699	21.559	21.387	21.216	20.990
R_1f_1	..	0.123	0.277	0.424	0.630
f_1	..	0.00646	0.01439	0.02256	0.032686
$R_1 = MR_D$..	19.03	19.27	19.06	19.28

TABLE IV

Succinic Acid in Diozan

No.	$f_1 \times 10^6$	ϵ	d	$\epsilon\alpha_2$	β
1	0	2.1921	1.01694
2	3,320	2.2126	1.01826	6.175	0.391
3	6,302	2.2295	..	5.935	..
4	7,250	2.2361	1.01981	6.069	0.389
5	10,592	2.2591	1.02106	6.326	0.383
6	10,635	..	1.02130	..	0.403
7	12,028	2.2683	..	6.335	..
8	12,470	2.2698	..	6.231	..

$T_{\infty}^P = 115.59$ c.c. $1.05 MR_D = 24.43$ c.c. (see Table V).
 $0^P = 91.16$ c.c. $\mu = 2.13$ D.

TABLE V

Molar Refraction of Succinic Acid in Diozan (Na D)

No.	$M_1f_1 + M_2f_2$	f_2	n_{12}	n_{12}^2	d	$R_1f_1 + R_2f_2$	R_2f_2	R_1f_1	f_1	R_1
1	88.06	1.00000	1.41532	2.00313	1.01694	21.699	21.699
2	88.27772	0.99275	1.41572	2.00426	1.01981	21.710	21.542	0.168	0.00725	23.18
3	88.37808	0.98941	1.41591	2.00480	1.02106	21.717	21.469	0.247	0.01059	23.35

TABLE VI
Glutaric Acid in Dioxan

No.	$f_1 \times 10^6$	ϵ	d	$\alpha\epsilon_2$	β
1	0	2.1922	1.01694
2	3,444	2.2198	1.01795	(8.014)	0.289
3	6,796	2.2439	1.01909	7.607	0.311
4	10,637	2.2734	1.02033	7.634	0.313
5	14,854	2.3050	1.02164	7.594	0.311

$T^P_\infty = 142.28$ c.c. $1.05 MR_D = 30.52$ c.c. (see Table VII).
 ${}_0P = 111.76$ c.c. $\mu = 2.36$ D.

TABLE VII
Molar Refraction of Glutaric Acid in Dioxan ($Na D$)

$M_1f_1 + M_2f_2$	88.06	88.21171	88.35936	88.52856	88.71432
f_2	1	0.99656	0.99320	0.98936	0.98515
n_{12}	1.41532	1.41553	1.41572	1.41597	1.41620
n_{12}^2	2.00313	2.00373	2.00426	2.00497	2.00562
d	1.01694	1.01795	1.01909	1.02033	1.02164
$R_1f_1 + R_2f_2$	21.699	21.724	21.754	21.772	21.805
R_2f_2	21.699	21.624	21.551	21.468	21.377
R_1f_1	..	0.100	0.203	0.304	0.428
f_1	..	0.00344	0.00680	0.01064	0.01485
R_1	..	29.08	29.85	28.55	28.80

TABLE VIII
Adipic Acid in Dioxan

No.	$f_1 \times 10^6$	ϵ	d	$\alpha\epsilon_2$	β
1	0	2.1922	1.01694
2	2,490	2.2116	1.01781	7.791	0.343
3	4,827	2.2305	1.01849	7.935	0.316
4	6,648	2.2438	1.01918	7.762	0.331
5	9,550	2.2627	1.01991	7.382	0.306

$T^P_\infty = 147.53$ c.c. $1.05 MR_D = 33.43$ c.c. (see Table IX).
 ${}_0P = 114.10$ c.c. $\mu = 2.39$ D.

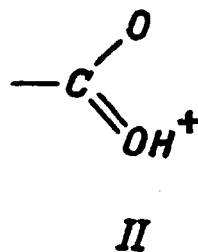
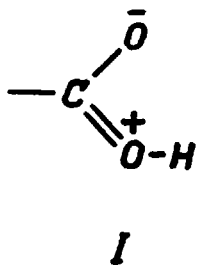
TABLE IX

Molar Refraction of Adipic Acid in Dioxan (Na D)

$M_1f_1 + M_2f_2$	88.06	88.34035	88.44612	88.61466
f_2	1	0.99517	0.99335	0.99045
n_{12}	1.41534	1.41561	1.41568	1.41602
n_{12}^2	2.00319	2.00395	2.00415	2.00511
d	1.01694	1.01849	1.01918	1.01991
$R_1f_1 + R_2f_2$	21.700	21.748	21.763	21.804
R_2f_2	21.700	21.595	21.556	21.493
R_1f_1	..	0.153	0.207	0.311
f_1	..	0.00483	0.00665	0.00955
R_1	..	31.72	31.16	32.63

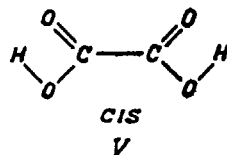
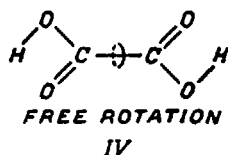
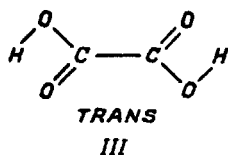
4. DISCUSSION

In order to calculate the moments of these dicarboxylic acids, a knowledge of the magnitude and direction of the resultant moment of the carboxyl group is essential. Using the bond moment values of $C=O = 2.3$ D, $C-O = 0.8$ D, $O-H = 1.5$ D and the values of 120° and 110° respectively for the angles $O-C-O$ and $C-O-H$, the resultant moment of $-COOH$ group comes out as nearly 1D acting in a direction almost perpendicular to the $-C$ bond. But this value is definitely lower since the dipole moments of formic acid and benzoic acid are 1.51 D (Zahn, 1931) and 1.74 D (Wilson and Wenzke, 1935; Brooks and Hobbs, 1940) respectively. The higher moment value of the carboxyl groups is possibly due to contributions from ionic structures arising from resonance. Zahn (1934) has discussed the various possible ionic structures for the carboxyl group and of these we may consider here I and II. Brooks and Hobbs (1940) have already pointed out that the effect of I is



such as to increase the resultant moment of the group. From a consideration of the dipole moments of benzoic acid and related derivatives these authors find that a group moment of 1.74 D may be ascribed to the $-COOH$ group, the resultant vector making an angle of 76° with the $-C$ bond. It may be pointed out here that the value calculated for the moment of formic acid on this basis is 1.59 D which is in good agreement with the experimental value of 1.51 D. We have therefore used the value of 1.74 D for the moment of the carboxyl group in all our subsequent calculations.

The moment of anhydrous oxalic acid has been calculated for the three probable structures (III, IV and V). Other structures involving rotation of the —OH group around the C—O bond of the carboxyl need not be considered here since it has been shown from studies of the temperature dependence of the dipole moments of fatty acids that such rotations are not present at ordinary temperatures (Meyer, 1930; Zahn, 1931). The calculated values of the moments for structures III, IV and V are 0 D, 2.39 D and 3.38 D respectively. The experimentally obtained value is 3.0 D in dioxan. A few remarks regarding the use of dioxan as a solvent for these dicarboxylic acids may not be out of place here. Wilson and Wenzke have claimed that μ_{dioxan} values are closer to μ_{gas} values for several monocarboxylic acids on account of the influence of dioxan in breaking up of hydrogen bonds of the dimers. However, this still leaves the possibility of interaction



*↻ represents rotation
around the bond*

between the solute molecules and dioxan. In fact, it has been pointed out by Le Fevre and Vine (1938) that μ_{dioxan} values may represent the properties of the solute-dioxan complex. Indications of such an interaction have already been obtained from dipole moment studies of another dicarboxylic acid, namely camphoric acid, in dioxan (Narasimhan and Ananthakrishnan, 1953). Considering the above facts and the high values of μ_{dioxan} in general, we may safely conclude that μ_{dioxan} values may be taken as the upper limit. In the case of anhydrous oxalic acid the observed value of 3.00 D therefore favours structure IV in which there is freedom of rotation around the C—C bond of the carboxyl groups. A slight increase in the calculated value of the molecule may be expected from the mutual interaction of the two carboxyl groups on account of their close proximity. In any event, it is obvious that structure III will lead only to a zero value for the moment of the molecule due to its symmetry and it is highly improbable that the solute-solvent interaction alone of this trans-structure will be able to account for the observed high moment value. Although the X-ray data of the crystalline anhydrous acid (Hendricks, 1935) show the molecule to be of the trans-form the evidence from dipole moment data of the solution cannot be satisfactorily interpreted on the basis of this structure. It is probable that by a dissolution in a non-polar solvent and at very high dilutions where the interaction between the individual solute molecules is negligible, the rotational freedom of the carboxyl groups around the C—C bond is restored. Further, it is of interest to note that Smyth and Walls (1931) have found that the observed moment of the diethyl oxalate is in agreement with the value calculated assuming free rotation around the C—C bond. The 'single bond' value obtained by Hendricks for the C—C distance in anhydrous oxalic acid and other oxalates is also in favour of this view since rotation is more probable around a 'single bond'.

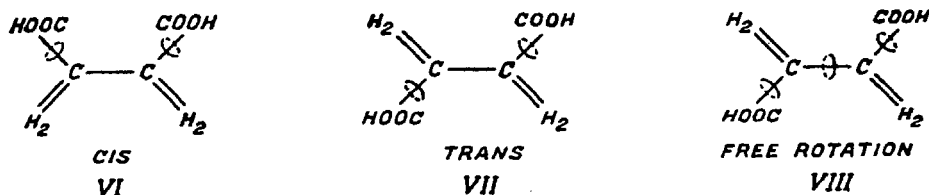
The angle between the resultant moment vectors of the two carboxyl groups is altered by the insertion of the —CH₂— group to form malonic acid. The moment value of this acid may be calculated on the assumption of free rotation of the carboxyl groups. The value thus obtained is highly dependent on the C—H bond moment value taken. Gent (1948) has shown that in aliphatic compounds

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the polarity of the C—H bond is C—H with a moment of 0.4 D. He has further

pointed out that the moment value of 0.4 D of this bond might be very much reduced under the electrostatic influence of strong polar groups. The calculated moment value of malonic acid will thus vary from 2.00 D-2.43 D as the

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C—H bond moment is altered from 0.4 D to 0 D. Bearing in mind the fact that μ_{dioxan} values are usually higher, the experimental value of 2.64 D in dioxan may be taken as favouring rotation of the carboxyl groups. With the addition of another —CH₂— group to form succinic acid we have the possibilities of cis-trans isomerism and free rotation. The assumption of free rotation of the carboxyl group in these acids has been already justified in the cases of oxalic and malonic acids and we may therefore consider the three probable structures VI, VII and VIII for succinic acid.



↻ represents rotation
around the bond

The values calculated for the moments of the three structures are VI = 1.66 D; VII = 2.38 D; VIII = 2.55 D. The calculated moment value for the cis-structure

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would vary from 1.66 D to 2.52 D as moment of the C—H bond is reduced from 0.4 to 0 D. On the other hand, the value for VIII would be reduced from 2.55 D to 2.40 D only for a corresponding change in the C—H bond moment. From observed moment value 2.13 D in dioxan it is very difficult to decide unambiguously between structures VI and VII. By an analogy with the ethyl ester of the acid for which Zahn (1932) has shown that the trans-structure is more probable we may conclude that the acid has the trans-form.

As we pass on from succinic acid to glutaric acid we find that the influence of the chain length is very much less, the difference in the moments being only 0.23 D. Assuming tetrahedral valence angles for the chain carbon atoms the moment of the molecule calculated for free rotation of the end carboxyl groups is 2.00 D which value may be slightly increased with the change in the C—H bond moment value. The fair agreement with the experimental value of 2.36 D in dioxan is therefore in favour of the assumption of free rotation of the carboxyl groups. Further lengthening of the chain has little influence on the dipole moments of these acids since we find the moment of adipic acid to be 2.39 D, the difference between the moments of glutaric acid and adipic acid being only 0.03 D, which is almost the limit of experimental error. The dipole moments of the corresponding ethyl esters also show the same behaviour, the moments of both diethyl glutarate and diethyl adipate being nearly 2.42 D (in benzene). The moment value for adipic acid obtained in the present investigation is very much lower than that reported by Tseng, Sun and Yao (1937). It may be pointed out here that their value of 4.04 D is extremely high and is inconsistent with the dipole moment data of the ethyl ester. The large value obtained by these authors may be due to high concentrations of the solutions employed or due to experimental error. Since their original paper is not available to the present author, he is unable to decide this point. The value of 2.39 D reported here for the acid is in conformity with the dipole moment of diethyl adipate and also with the moments of the other acids of this series.

Except in the cases of the oxalate and the corresponding acid, the moments of the ethyl esters of the dicarboxylic acids and the acids themselves follow the same sequence. Thus malonate > succinate < glutarate > adipate and malonic acid > succinic < glutaric > adipic. Gane and Ingold (1928) have determined the first (K_1) and second (K_2) dissociation constants of these dicarboxylic acids electrometrically and their values have been compared with the dipole moments of these acids in Table X. Nathan and Watson (1933) have shown that the dissociation constants of acids of the type $XCH_2 \cdot COOH$ may be quantitatively related by the equation $\log_e K = \log_e K_0 - 2.4 (\mu + 0.032\mu^2)$ where K_0 is the dissociation constant of acetic acid and μ is the dipole moment of CH_2X .

TABLE X
Dipole Moments and Dissociation Constants of Dicarboxylic Acids

	$K_1 \times 10^6$	$K_2 \times 10^6$	μ (D)	$\log_e K_1$	$\log_e K_2$	$\log_e K$ (calcd.)
Oxalic	3.00
Malonic	17.7	4.37	2.64	-14.37	-15.27	-14.44
Succinic	0.74	4.50	2.13	-13.50	-15.30	-14.91
Glutaric	0.46	5.34	2.36	-13.00	-15.47	-15.74
Adipic	0.39	5.29	2.39	-12.86	-15.46	..

Thus, for example, the value of $\log_e K$ for malonic acid could be calculated by substituting the value of 1.49 D for the μ of acetic acid while the value of $\log_e K$ for succinic acid could be calculated by using the value of 1.59 D for the μ of propionic acid (μ values taken from Tables of Dipole Moments, 1934). The results are given in Table X where it is seen that the calculated values of $\log_e K$ are in fair agreement with the experimental values. In calculating the $\log_e K$ value of glutaric acid we have used the value of 1.90 D for butyric acid (in benzene) given by Pohl, Hobbs and Gross (1940) while the previous μ values are from measurements on the gas.

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