DIPOLE MOMENTS OF AROMATIC CARBOXYLIC ACIDS

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Abstract

The dipole moments of phthalic, α- and β-naphthoic acids in dioxan have been determined. Schenkel's correlation of the moment of an aromatic carboxylic acid with the π-electron density distribution of the parent hydrocarbon has been discussed in the light of the new data. The relation between the moment values of isomeric acids and their dissociation constants has also been examined.

1. Introduction

Using the dipole moment data on the methyl esters of aromatic carboxylic acids published by Lauer (1937), Schenkel (1948) has found a close parallelism between the π-electron density of the parent hydrocarbon and the dipole moment as well as the dissociation constants of these acids. The present investigation on the dipole moments of phthalic, α- and β-naphthoic acids was started since it was felt that it would be better to use the dipole moment data on the acids themselves instead of the data on the esters. Unfortunately, the solubility of several of the aromatic carboxylic acids even in dioxan was so low that they had to be left out. However, the data obtained on the three carboxylic acids mentioned above were sufficient enough to allow the desired comparison. The details are presented below.

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 $= 101 \cdot 5°$; $d_4{}^{35} = 1 \cdot 01694$; $n_D{}^{35} = 1 \cdot 41532$.

The carboxylic acids used were "Kahlbaum pure" products. They were recrystallized several times from absolute ethyl alcohol, the melting points of α- and β-naphthoic acids being $161°$ and $186°$ respectively. (The melting point of phthalic acid was not sharp owing to decomposition of the acid near m.pt.) Details of the apparatus used for the measurement of dielectric constants have been already given by the author in an earlier publication (Narasimhan, 1953). A constant voltage transformer was used to supply A.C. voltage for the measuring unit. The test cell used was of the Sayce-Briscoe type. Measurements of densities were carried out with an Ostwald-Sprengel pyknometer. All measurements have been made at a temperature of $35°$ C.

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3. RESULTS

For the computation of the dipole moments of the acids from the dielectric constant and density data on dilute solutions the mathematical extrapolation method of Hedestrand (1929) has been employed. Molar refraction has been calculated by the use of addition of atomic as well as bond refractivities (Bauer, 1949; Denbigh, 1940). Atom polarisation was taken as 5% of the molar refraction (MR_n). The results obtained are given in Tables I-III.

TABLE I

Phthalic 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	1,988	2·2065	1·01800	7·202	0·524
3	5,424	2·2312	1·01988	7·191	0·533
4	9,460	2·2604	1·02205	7·211	0·532
5	12,134	2·2794	1·02356	7·189	0·537

Total Polarisation $T_\infty P = 140\cdot29$ c.c. $1\cdot05\ MR_D$ (calcd.) $= 35\cdot07$ c.c.
Orientation Polarisation $_0P = 105\cdot22$ c.c. $\mu = 2\cdot30$ D.

TABLE II

α-Naphthoic Acid in Dioxan

No.	$f_1 \times 10^6$	ϵ	d	$\alpha \epsilon_2$	β
1	0	2·1922	1·01694	..	..
2	2,660	2·2060	1·01762	5·188	0·598
3	3,584	2·2108	1·01913	5·190	0·600
4	5,890	2·2232	1·02037	5·263	0·592
5	6,066	2·2237	1·02058	5·193	0·590

$T_\infty P = 110\cdot94$ c.c. $1\cdot05\ MR_D$ (calcd.) $= 41\cdot09$ c.c.
$_0P = 69\cdot85$ c.c. $\mu = 1\cdot87$ D.

TABLE III

β-Naphthoic Acid in Dioxan

No.	$f_1 \times 10^6$	ϵ	d	$a\epsilon_2$	β
1	0	2·1922	1·01694	..	..
2	4,041	2·2144	1·01918	5·520	0·546
3	7,298	2·2331	1·02102	5·604	0·550
4	12,587	2·2615	1·02411	5·506	0·560
5	18,272	2·2951	1·02722	5·510	0·553

$T_{\infty}P = 117\cdot00$ c.c. $1\cdot05\ MR_D$ (calcd.) $= 41\cdot09$ c.c.

$_0P = 75\cdot91$ c.c. $\mu = 1\cdot95$ D.

4. Discussion

The dipole moment of dimethyl phthalate has been previously determined by Weissberger and Williams (1929) as 2·8 D. The lower value of 2·3 D obtained for the acid may be qualitatively accounted for on the basis of the " ortho-effect " as well as mesomeric effects. The dipole moments of α- and β-naphthoic acids are very close to that of benzoic acid in dioxan (*viz.*, 1·74 D; Refer Wilson and Wenzke, 1935; also Brooks and Hobbs, 1940). The slightly larger value for β-naphthoic acid is in accordance with the dipole moment data on the methyl esters but the difference between the α- and β-acids is not as high as in the corresponding esters. From the resonance point of view this state of affairs can be better understood since resonance in the carboxyl group will tend to be more complete than in the ester and thus the π-electron density distribution will be less uneven. It is now possible to study this aspect of the problem more quantitatively in the light of the π-electron density distribution of the parent hydrocarbon, namely, naphthalene, obtained by quantum mechanical methods. We shall discuss this point accordingly here.

Schenkel (1948) has calculated the π-electron densities of the substituted carbon atoms corresponding to the α- and β-positions of naphthalene. The values are respectively 0·148 and 0·076. The dissociation constants of α- and β-naphthoic acids are respectively $2\cdot03 \times 10^{-4}$ and $0\cdot68 \times 10^{-4}$ while the dipole moments of the methyl esters are 1·51 D and 1·71 D respectively. On the other hand, the dipole moments of the corresponding acids themselves are 1·87 D and 1·95 D (in dioxan). Although the lower π-electron density in the β-compound corresponds to a higher moment value and a lower dissociation constant the observed difference in the moment values of the two isomeric acids is indeed very small. The introduction of the carboxyl group will certainly

alter the π-electron density distribution of the naphthalene ring and it is therefore inadequate to make comparisons with the parent hydrocarbon. It is however possible to calculate the charge distribution in the substituted hydrocarbon by using perturbation theory (Wheland and Pauling, 1935) but our qualitative knowledge regarding the perturbation parameter for the carboxyl group does not warrant such calculations.

It is interesting to note here that more than the dipole moment the dissociation constants of the naphthoic acids are very sensitive to the positional isomerism. This appears to be so only in the case of the naphthalene carboxylic acids while in anthracene carboxylic acids the dissociation constants for 1 and 9 substituted acids are very close ($2 \cdot 06 \times 10^{-4}$ and $2 \cdot 26 \times 10^{-4}$ respectively). Although the moment data on other aromatic carboxylic acids are essential for a complete study of the relation between the dissociation constant, charge distribution and dipole moment of these acids it is clear that a correlation between the dipole moment of the *acid* and the charge distribution of the *parent hydrocarbon* is probably not fully justifiable. The extremely low solubility of many of the aromatic carboxylic acids in usual non-polar solvents presents a serious problem in this field of study. Owing to this reason data on three acids alone have been reported here.

The author's grateful thanks are due to Prof. R. S. Krishnan for his valuable help and guidance in the progress of this work.

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