Studies on the Intramolecular Hydrogen Bond in Conjugated Systems by the Measurements of Dipole Moments. II. Salicylaldehyde and o-Hydroxyacetophenone

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Introduction

It is well known from infrared absorption spectra that salicylaldehyde and *o*-hydroxyacetophenone have no free hydroxyl groups and hence all the molecules form intramolecular hydrogen bonds[1]. In the previous paper[2], the present authors discussed the magnitudes and the directions of charge migrations caused by the hydrogen bonding in an *o*-nitrophenol molecule. Since a similar charge migration due to the intramolecular hydrogen bonding is also expected in the case of salicylaldehyde and *o*-hydroxyacetophenone molecules, it would be of interest to determine its magnitude and direction. The same treatment as that of *o*-nitrophenol can be applied to these two compounds.

Experimental

Materials.—All the materials were prepared in the present authors' laboratory except *p*-chloroacetophenone, *p*-nitroacetophenone and 5-chloro-2-hydroxybenzaldehyde which were purchased. 5-Chloro-2-hydroxybenzaldehyde, 5-methyl-2-hydroxybenzaldehyde and *p*-nitroacetophenone were purified by recrystallization, while

1) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York (1940), pp. 318, 319.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF THE DERIVATIVES OF SALICYLALDEHYDE AND ACETOPHENONE IN BENZENE SOLUTIONS

Compounds	$w \times 10^5$	ε	d
4-Chloro-2-hydroxybenzaldehyde (m. p. 52°)	130	2.2693	0.86692
	240	2.2726	0.86723
	597	2.2869	0.86839
	690	2.2905	—
5-Chloro-2-hydroxybenzaldehyde (m. p. 100°)	395	2.2677	0.86771
	616	2.2710	0.86837
	1198	2.2793	0.87017
	1748	2.2867	0.87188
5-Methyl-2-hydroxybenzaldehyde (m. p. 55°)	124	2.2850	0.87202
	207	2.2924	0.87248
	298	2.3014	0.87283
p-Chloroacetophenone (b. p. 232°)	366	2.2791	0.86817
	1137	2.3074	0.86987
	2568	2.3659	0.87321
	4460	2.4432	0.87774
p-Nitroacetophenone (m. p. 80°)	215	2.2785	0.86716
	485	2.2972	—
	870	2.3252	0.86888
	1876	2.3953	0.87185
5-Chloro-2-hydroxyacetophenone (m. p. 54°)	271	2.2693	0.86753
	574	2.2754	0.86841
	1813	2.3004	0.87195
	3750	2.3410	0.87741

TABLE II

MOLECULAR POLARIZATIONS AND DIPOLE MOMENTS OF THE DERIVATIVES OF SALICYLALDEHYDE AND ACETOPHENONE IN BENZENE SOLUTIONS

Compounds	t(°C)	ε_1	d_1	α	β	$P_{2\infty}$	MR_D	μ(D)
4-Chloro-2-hydroxybenzaldehyde	30	2.2639	0.86649	3.85	0.317	148.6	38.5	2.31
5-Chloro-2-hydroxybenzaldehyde	30	2.2623	0.86648	1.40	0.309	76.3	38.5	1.37
5-Methyl-2-hydroxybenzaldehyde	25	2.2732	0.87147	9.43	0.464	263.9	38.1	3.32
p-Chloroacetophenone	30	2.2630	0.86725	4.03	0.234	157.1	40.4	2.40
p-Nitroacetophenone	30	2.2634	0.86650	7.04	0.283	259.4	42.2	3.29
5-Chloro-2-hydroxyacetophenone	30	2.2635	0.86678	2.06	0.284	106.2	41.9	1.79

4-chloro-2-hydroxybenzaldehyde and 5-chloro-2-hydroxyacetophenone were purified by steam distillation followed by recrystallization. *p*-Chloroacetophenone was purified by distillation.

Measurements.—All the measurements were made in benzene solutions at 30°C or 25°C. The apparatus and the method of measurements were the same as those used in the previous study[2]. Halverstadt-Kumler's method was employed throughout.

Results.—The results are shown in Table I and Table II, in which notations have the same significance as those used in the previous paper.

Results and Discussions

It was shown in the previous paper[2] that unless there is hydrogen bonding or a special steric effect between the substituents the dipole moments of benzene derivatives having certain substituents can be expressed by the vector sum of the group moments of the respective substituents within 0.1 D. In order to discuss the dipole moments of salicylaldehyde and *o*-hydroxyacetophenone, therefore, it is necessary to obtain the moments of aldehyde and acetyl groups which are required for calculating the dipole moments of the hypothetical salicylaldehyde and *o*-hydroxyacetophenone molecules having no intramolecular hydrogen bonds.

Since it is known that benzaldehyde and acetophenone molecules are planar[3], let the molecules be placed in a coordinate system as in Fig. 1. The x- and y-components of the dipole moment of benzaldehyde are denoted by μ_{x1} and μ_{y1} and

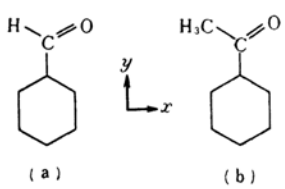


Fig. 1

TABLE III

DIPOLE MOMENTS OF BENZALDEHYDE, ACETOPHENONE AND THEIR DERIVATIVES IN BENZENE SOLUTIONS

Compounds	$\mu_{obs.}$(D)	$\mu_{calcd.}$(D)	$\Delta\mu$(D)
Benzaldehyde	2.96[4]	3.00	+0.04
p-Fluorobenzaldehyde	1.96[5]	2.02	+0.06
p-Chlorobenzaldehyde	2.03[4]	1.97	−0.06
p-Methylbenzaldehyde	3.30[6]	3.33	+0.03
p-Nitrobenzaldehyde	2.41[4]	2.41	0.00
Acetophenone	2.96[7]	2.96	0.00
p-Chloroacetophenone	2.40	2.37	−0.03
p-Methylacetophenone	3.23[7]	3.22	−0.01
p-Nitroacetophenone	3.29	3.22	−0.07

those of *o*-hydroxyacetophenone by μ_{x2} and μ_{y2}, respectively. The second column of Table III shows the observed moments, $\mu_{obs.}$, of benzaldehyde, acetophenone and their derivatives in benzene solutions. The two components of the moment of benzaldehyde, μ_{x1} and μ_{y1}, must satisfy the following five equations, since the dipole moment of fluorobenzene is 1.48 D, that of chlorobenzene 1.60 D, that of toluene 0.4 D, and that of nitrobenzene 4.0 D in benzene solutions.

$$\mu_{x1}^2+\mu_{y1}^2=(2.96)^2 \quad \text{(for benzaldehyde)} \tag{1}$$

$$\mu_{x1}^2+(\mu_{y1}-1.48)^2=(1.96)^2 \quad \text{(for } p\text{-fluorobenzaldehyde)} \tag{2}$$

$$\mu_{x1}^2+(\mu_{y1}-1.6)^2=(2.03)^2 \quad \text{(for } p\text{-chlorobenzaldehyde)} \tag{3}$$

$$\mu_{x1}^2+(\mu_{y1}+0.4)^2=(3.30)^2 \quad \text{(for } p\text{-methylbenzaldehyde)} \tag{4}$$

$$\mu_{x1}^2+(\mu_{y1}-4.0)^2=(2.41)^2 \quad \text{(for } p\text{-nitrobenzaldehyde)} \tag{5}$$

The two components of acetophenone, μ_{x2}

2) B. Eda and K. Ito, This Bulletin, **29**, 524 (1956).
3) W. Klyne, "Progress in Stereochemistry", Butterworths Scientific Publications, London (1954), p. 148.
4) D. I. Coomber and J. R. Partington, *J. Chem. Soc.*, **1938**, 1444.
5) N. J. Leonard and L. E. Sutton, *J. Am. Chem. Soc.*, **70**, 1564 (1948).
6) J. N. Pearce and L.F. Berhenke, *J. Phys. Chem.*, **39**, 1005 (1935).
7) J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, **1949**, 2963.

end μ_{y2}, have to satisfy the following four aquations.

$$\mu_{x2}^2+\mu_{y2}^2=(2.96)^2 \quad \text{(for acetophenone)} \tag{6}$$

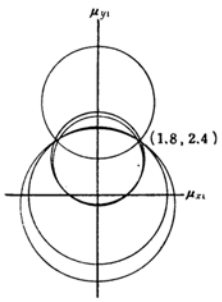
$$\mu_{x2}^2+(\mu_{y2}-1.6)^2=(2.40)^2 \quad \text{(for } p\text{-chloroacetophenone)} \tag{7}$$

$$\mu_{x2}^2+(\mu_{y2}+0.4)^2=(3.23)^2 \quad \text{(for } p\text{-methylacetophenone)} \tag{8}$$

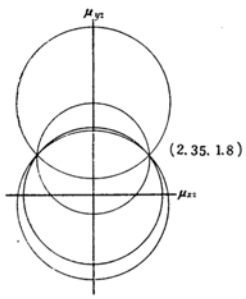
$$\mu_{x2}^2+(\mu_{y2}-4.0)^2=(3.29)^2 \quad \text{(for } p\text{-nitroacetophenone)} \tag{9}$$

It is known that the nitro group is not suitable for the treatment of vector summation because it has a large mesomeric interaction with other substituents. But in this case, *p*-nitrobenzaldehyde was chosen because the interaction of the nitro group with the aldehyde group is smaller than those of halogens[5].

When these equations were solved graphically it was found that the circles intersect each other almost at a point as illustrated in Fig. 2 and Fig. 3. Thus μ_{x1}, μ_{y1}, μ_{x2} and μ_{y2} were determined as ±1.8D, 2.4 D, ±2.35 D and 1.8 D, respectively. Of



benzaldehyde
Fig. 2



acetophenone
Fig. 3

the double sign of these values, the plus sign is reasonable. When these values were used for calculating the dipole moments of benzaldehyde, acetophenone and their derivatives, good agreements were found between the observed and calculated moments as shown in the third and fourth columns of Table III.

The *x*- and *y*-components, $\mu_{xI(calcd.)}$ and $\mu_{yI(calcd.)}$*, of a hypothetical salicylaldehyde molecule having no intramolecular hydrogen bond were calculated by the use of the components of the moment of benzaldehyde and those of the moment of phenol[2]. The values of $\mu_{xI(calcd.)}$ and $\mu_{yI(calcd.)}$ were calculated to be −0.4 D and

* In this paper, the suffixes I and II attached to μ refer to salicylaldehyde and *o*-hydroxyacetophenone, respectively.

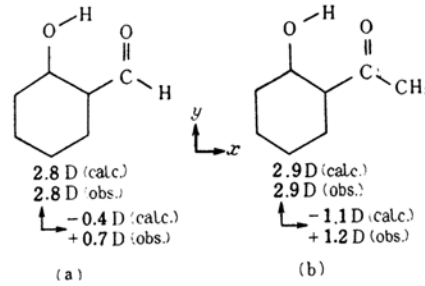


Fig. 4

+2.8 D, respectively. (See Fig. 4a). For the purpose of obtaining the *x*- and *y*-components of the dipole moment of a real salicylaldehyde molecule which has the intramolecular hydrogen bond, it is required to determine the components which satisfy the observed moments of salicylaldehyde, 4-chloro-2-hydroxybenzaldehyde, 5-chloro-2-hydroxybenzaldehyde and 5-methyl-2-hydroxybenzaldehyde. These values, $\mu_{xI(obs.)}$ and $\mu_{yI(obs.)}$, were determined to be +0.7 D and +2.8 D, respectively. As shown in Table IV, these two components give good agreement between the observed and calculated moments of the derivatives of salicylaldehyde.

TABLE IV
DIPOLE MOMENTS OF SALICYLALDEHYDE AND ITS DERIVATIVES IN BENZENE SOLUTIONS

Compounds	$\mu_{obs.}$ (D)	$\mu_{calcd.}$ (D)	$\Delta\mu$ (D)
Salicylaldehyde	2.88[8]	2.89	+0.01
4-Chloro-2-hydroxybenzaldehyde	2.31	2.20	−0.11
5-Chloro-2-hydroxybenzaldehyde	1.37	1.39	+0.02
5-Methyl-2-hydroxybenzaldehyde	3.32	3.28	−0.04

When the two components of salicylaldehyde, $\mu_{xI(obs.)}$ and $\mu_{yI(obs.)}$, are compared with the calculated components, $\mu_{xI(calcd.)}$ and $\mu_{xI(calcd.)}$, it is found that the difference is 1.1 D in the *x*-direction and 0.0 D in the *y*-direction. Presumably this difference is due mainly to the intramolecular hydrogen bond between the hydroxyl group and the carbonyl group, because it is greater than the errors inherent to the vector summation, the errror being estimated to be within 0.1 D for such molecules as given in Table III and Table IV of the previous paper[2] and in Table III of the present paper. If it is assumed from the consideration of the inaccuracy of the present method of approximation that μ_{x1} is 1.75～1.9 D and μ_{y1} is 2.3～2.5 D instead of μ_{x1}=

8) B. C. Curran, *J. Am. Chem. Soc.*, **67**, 1835 (1945).

1.8D and $\mu_{y1}=2.4$D, it is found that $\mu_{xI(calcd.)}$ and $\mu_{yI(calcd.)}$ are $-0.3\sim-0.5$ D and $2.7\sim2.8$ D, respectively. The difference turns out to be $1.0\sim1.2$ D in the x-direction and $0.0\sim0.1$ D in the y-direction. The conclusion is unaltered that the difference is great in the x-direction whereas there is little difference in the y-direction.

The dipole moment of *o*-hydroxyacetophenone can be discussed in a similar way. The calculated components of *o*-hydroxyacetophenone, which were assumed to be those of a hypothetical molecule having no hydrogen bond, were obtained from the components of phenol and the aforementioned x- and y-components of acetophenone, μ_{x2} and μ_{y2}. They are -1.1 D for $\mu_{xII(calcd.)}$ and $+2.9$ D for $\mu_{yII(calcd.)}$. (See Fig. 4b). The components of the dipole moment of a real *o*-hydroxyacetophenone molecule are those satisfying the observed moments 3.16 D[8] of *o*-hydroxyacetophenone and 1.79 D of 5-chloro-2-hydroxyacetophenone. They are determined to be ±1.2 D for $\mu_{xII(obs.)}$ and 2.9 D for $\mu_{yII(obs.)}$ as shown in Fig. 4(b). The sign of $\mu_{xII(obs.)}$ can be determined to be plus in analogy to salicylaldehyde. When these components, $\mu_{xII(obs.)}$ and $\mu_{yII(obs.)}$, are compared with $\mu_{xII(calcd.)}$ and $\mu_{yII(calcd.)}$ respectively, the difference is 2.3 D in the x-direction and 0.0 D in the y-direction. That is to say, there is a large difference only in the x-direction, which is definitely beyond the errors attributable to the vector summation. In the same manner as in salicylaldehyde, it will be necessary to make allowance for the degree of inaccuracy in μ_{x2} and μ_{y2}. If it is assumed that μ_{x2} is $2.35\sim2.4$ D and μ_{y2} is $1.75\sim1.8$ D, the calculated components of the hypothetical molecule having no hydrogen bond are $-1.1\sim-1.2$ D for $\mu_{xII(calcd.)}$ and $2.9\sim3.0$ D for $\mu_{yII(calcd.)}$. Therefore, the difference is $2.3\sim2.4$ D in the x-direction and $0.0\sim0.1$ D in the y-direction. Again the difference is great only in the x-direction.

The results mentioned above show that the charge migrations caused by the intramolecular hydrogen bond are from the hydroxyl oxygen to the carbonyl oxygen and their magnitudes are about 1.1 D in salicylaldehyde and about 2.3 D in *o*-hydroxyacetophenone. On the basis of the fact that the charge migration is caused mainly in the x-direction and is almost zero in the y-direction for the compounds in question, it is concluded that the contribution of the resonance structure shown in Fig. 5 is increased greatly and that its degree is about 10 to 20%. It is

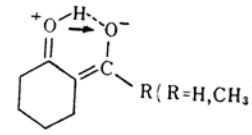


Fig. 5

very interesting that there is a remarkable difference between the magnitude of salicylaldehyde and that of *o*-hydroxyacetophenone. Anyway, it should be emphasized that the charge migration in the x-direction is great, or in other words, that the contribution of the resonance structure as shown in Fig. 5 due to the intramolecular hydrogen bond is indubitable.

Summary

Dipole moments of 4-chloro-2-hydroxybenzaldehyde, 5-chloro-2-hydroxybenzaldehyde, 5-methyl-2-hydroxybenzaldehyde, *p*-chloroacetophenone, *p*-nitroacetophenone and 5-chloro-2-hydroxyacetophenone were measured in benzene solutions. Their values are 2.31 D, 1.37 D, 3.32 D, 2.40 D, 3.29 D and 1.79 D, respectively. The components of the dipole moments of salicylaldehyde and *o*-hydroxyacetophenone, which were evaluated from the components of the moments of phenol, benzaldehyde and acetophenone, do not agree at all with the components that satisfy the observed moments of salicylaldehyde and *o*-hydroxyacetophenone and their derivatives. The magnitudes of the discrepancies are about 1.1 D in the x-direction for salicylaldehyde, about 2.3 D in the x-direction for *o*-hydroxyacetophenone, and almost 0.0 D in the y-direction for both compounds. It was concluded that the charge migration was caused from the hydroxyl oxygen to the carbonyl oxygen by the intramolecular hydrogen bonding.

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