Studies on the Intramolecular Hydrogen Bond in Conjugated Systems by the Measurements of Dipole Moments. I. o-Nitrophenol

By Bunzo EDA and Kazuo ITO

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Introduction

When a molecule having conjugated double bonds forms an intramolecular hydrogen bond, it is expected that the charge migration is caused by the bonding in the molecule. But the magnitude and direction of the migration have not been determined experimentally as yet. For the purpose of obtaining these, we measured the dipole moments of several compounds. In this paper we report the results obtained on *o*-nitrophenol.

From the infrared absorption spectrum it has been found that *o*-nitrophenol has no free hydroxyl group and consequently all the molecules form the intramolecular hydrogen bond[1]. In order to get information on the charge migration caused by the hydrogen bond in the molecule, it is necessary to compare the dipole moment of *o*-nitrophenol with the moment of a hypothetical *o*-nitrophenol molecule having no intramolecular hydrogen bond in regard to the directions of moments as well as their absolute values. The components of the dipole moment of *o*-nitrophenol can be obtained from the measurements of the dipole moments of *o*-nitrophenol, 4-chloro-2-nitrophenol and 4-methyl-2-nitrophenol, while the components of the dipole moment of the hypothetical *o*-nitrophenol having no hydrogen bond can be obtained from the sum of the respective components of the dipole moments of phenol and nitrobenzene. The order of magnitude of errors due to the assumption that the dipole moment of a molecule can be expressed by the vector sum of bond moments was estimated with the aid of the dipole moments of anisole and its derivatives.

Experimental

Materials.—All the materials were prepared in our laboratory except *o*-nitrophenol and 4-chloro-2-nitroanisole which were purchased and purified by recrystallization. 4-Chloro-2-nitrophenol and 4-methyl-2-nitrophenol were purified by steam distillation followed by recrystallization, while *o*-nitroanisole was purified by vacuum distillation.

Measurements.—All the measurements were made in benzene solutions at 25°C. The dielectric constants were measured by heterodyne beat method. A modified Hedestrand method was employed for obtaining the specific polarization at infinite dilution. The method was similar to that introduced by Halverstadt and Kumler[2], differing in that densities were used rather than the specific volumes. The sum of electronic polarization and atomic polarization was assumed to be equal to the molecular refraction for D-line calculated additively from the atomic refractions of the constituent atoms.

Results.—The results are shown in Table I and II, where μ is the dipole moment in Debye unit. All the notations have the same significances as those used by Kurita et al.[3]. The data found in literatures to be compared with the present results are those of Jenkins on *o*-nitrophenol[4] and of Cowley and Partington on *o*-nitroanisole[5].

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

[2] I.F. Halverstadt and W.D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[3] Y. Kurita, T. Nozoe and M. Kubo, This Bulletin, **26**, 242 (1953).

[4] H.O. Jenkins, *J. Chem. Soc.*, **1936**, 1049.

[5] E.G. Cowley and J.R. Partington, *J. Chem. Soc.*, **1933**, 1257.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES IN BENZENE SOLUTIONS OF *o*-NITROPHENOL, *o*-NITROANISOLE AND THEIR DERIVATIVES AT 25°C

Compounds	$w \times 10^5$	ε	d
o-Nitrophenol	138	2.2825	0.87169
(m. p. 45°)	777	2.3328	0.87372
	1681	2.4050	0.87642
	3019	2.5110	0.88040
4-Chloro-2-nitrophenol	295	2.2836	0.87211
(m. p. 86°)	594	2.2943	0.87331
	1172	2.3144	0.87516
	2741	2.3717	0.88096
4-Methyl-2-nitrophenol	214	2.2928	0.87192
(m. p. 32°)	778	2.3401	0.87329
	1664	2.4183	0.87565
	2913	2.5272	0.87904
o-Nitroanisole	152	2.2971	0.87130
(b. p. 165° at 39 mmHg)	331	2.3271	0.87182
	520	2.3598	0.87239
	765	2.3991	0.87307
4-Chloro-2-nitroanisole	302	2.3117	0.87344
(m. p. 98°)	496	2.3360	0.87413
	824	2.3761	0.87503

TABLE II

MOLECULAR POLARIZATIONS AND DIPOLE MOMENTS OF *o*-NITROPHENOL, *o*-NITROANISOLE AND THEIR DERIVATIVES IN BENZENE SOLUTIONS AT 25°C

Compounds	ε_1	d_1	α	β	$P_{2\infty}$	MR_D	μ
o-Nitrophenol	2.2714	0.87132	7.94	0.301	239.4	34.4	3.16
4-Chloro-2-nitrophenol	2.2727	0.87106	3.60	0.360	152.8	39.3	2.35
4-Methyl-2-nitrophenol	2.2734	0.87129	8.71	0.265	287.8	39.2	3.49
o-Nitroanisole	2.2720	0.87086	16.68	0.290	517.2	39.2	4.83
4-Chloro-2-nitroanisole	2.2746	0.87248	12.33	0.314	476.3	44.0	4.60

Their values of 3.11 D and 4.83 D respectively are in good agreement with ours.

Discussion

The near-ultraviolet absorption spectra of phenol and anisole in cyclohexane solutions[6] agree with each other to a high degree of precision both in the wavelengths of maximum absorption and in intensities. Moreover, the resonance energy of phenol is almost the same as that of anisole[7]. Accordingly, if the observed moments of anisole, its *ortho*- and *para*-derivatives and the *para*-derivative of *o*-nitroanisole are fairly consistent with those calculated by vector addition, it will be reasonable to suppose that the method of vector sum of bond moments can also be used with nearly the same accuracy in the corresponding phenol derivatives.

Let it be assumed that the methoxy group is in the plane of an anisole molecule as illustrated in Fig. 1 (a). The components of dipole moment in x- and y-directions are

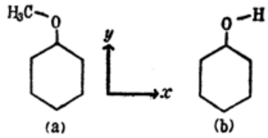

Fig. 1.

denoted by μ_x and μ_y, respectively. Since the observed moment of anisole in benzene solution is 1.28 D[8] we have

$$\mu_x^2+\mu_y^2=1.28^2 \tag{1}$$

The mesomeric moment from the methoxy group to benzene ring is, of course, included in these two components. The dipole moment of hydroquinone dimethylether $C_6H_4(OCH_3)_2$ would have the same value[9], which is equal to $\sqrt{2}\mu_x$, whether (i) the methoxy groups rotate freely, (ii) they are fixed in equally probable *cis*- and *trans*-forms, (iii) the groups in these *cis*- and *trans*-forms rotate freely within certain limits of angle, or (iv) the oscillation, not being free, is such that the probability of any angle, of swing is some function of that angle, the same function applying to each group. The observed moment in benzene solution is 1.73 D[8], hence μ_x is ±1.2 D. As it is most probable that the direction is $H_3{}^{+}C\text{–}O^{-}$, we prefer $\mu_x=+1.2$ D. Putting it in (1), we get $\mu_y=\pm0.4$ D. If we use the components $\mu_x=+1.2$ D and $\mu_y=-0.4$ D, the calculated moments of anisole, its *ortho*- and *para*-derivatives and 4-chloro-2-nitroanisole agree with the observed ones to within less than 0.1 D as shown in Table III. Therefore, the moments of anisole, its *ortho*- and *para*-derivatives and the *para*-derivative of *o*-nitroanisole can be expressed by the vector sum to within less than 0.1 D including the difference in mesomeric effect and solvent effect unless they are compelled to be in the other particular configuration by

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[6] R.A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds", John Wiley & Sons, Inc., New York (1951); Fig. 31 and Fig. 55.

[7] G.W. Wheland, "The Theory of Resonance", John Wiley and Sons, Inc., New York (1944), p. 69.

[8] K.B. Everard and L.E. Sutton, *J. Chem. Soc.*, **1949**, 2312.

[9] K.B. Everard and L.E. Sutton, *J. Chem. Soc.*, **1951**, 19.

TABLE III

DIPOLE MOMENTS OF ANISOLE DERIVATIVES IN BENZENE SOLUTIONS

Substituents	$\mu_{calcd.}$ (D)$^{a,b)}$	$\mu_{obs.}$(D)$^{c)}$
p–CH_3	1.20	1.20
p–Br	2.31	2.23
p–Cl	2.33	2.24
o–F	2.50*	2.31
o–Cl	2.60	2.50
o–Br	2.58	2.47
o–CH_3	1.05	1.0
o–NO_2	4.92	4.83
4–Cl–2–NO_2	4.66	4.60

a) The bond moments of the substituents are based on the following data[10], bromobenzene 1.57 D, chlorobenzene 1.60 D, fluorobenzene 1.48 D, toluene 0.4 D and nitrobenzene 4.0 D in benzene solutions.

b) In *ortho*-derivatives it is assumed that the methoxy group is fixed in the molecular plane and the methyl carbon is in the side opposite to *ortho*-substituent.

c) The observed values were taken from "Tables of Electric Dipole Moments"[11] except those of o-nitroanisole and 4-chloro-2-nitroanisole.

* The difference for o-fluoroanisole is greater because the small size of the fluorine atom makes the *cis*-configuration less improbable for this compound than for the other *ortho*-substituted anisoles.

steric hindrance, etc. Likewise, were it not for the hydrogen bond or a remarkable change of configuration, it should be possible to express the dipole moments of phenol, its *para*-derivatives and *ortho, para*-disubstituted derivatives by the vector sum to within less than 0.1 D.

The x- and y-components of dipole moment of phenol, Fig. 1 (b), can be obtained from the moment of phenol and its *para*-derivatives. If it is assumed that $\mu_x=1.55$ D and $\mu_y=0.0$ D, the observed moments agree with the calculated ones as shown in Table IV. On the contrary, the calculated moments of o-nitrophenol, 4-chloro-2-nitrophenol and 4-methyl-2-nitrophenol do not agree with the observed ones by the order of 0.4 D as shown in Table V. These discrepancies are definitely greater than those in Table III and IV. Since all the compounds given in Table V are supposed to have an intramolecular hydrogen bond between the hydroxyl group and the nitro group, this abnormality may be due mainly to the hydrogen bond. The components of o-nitrophenol that satisfy the observed moments of o-nitrophenol, 4-chloro-2-nitrophenol and 4-methyl-2-nitrophenol are $\mu_x=2.2$–2.3 D and $\mu_y=2.2$–2.35 D, respectively. The calculated components based on the aforementioned components of phenol and the dipole moment of nitrobenzene are $\mu_{x\ calcd.}=1.9$ D and $\mu_{y\ calcd.}=2.0$ D, respectively. Hence we have $\Delta\mu_x=0.3$–0.4 D and $\Delta\mu_y=0.2$–0.35 D as the abnormal values.

TABLE IV

DIPOLE MOMENTS OF PHENOL AND ITS *para*-DERIVATIVES IN BENZENE SOLUTIONS

Compounds	$\mu_{calcd.}$(D)	$\mu_{obs.}$(D)$^{a)}$	$\Delta\mu$(D)$^{b)}$
Phenol	1.55	1.56	+0.01
p-Bromophenol	2.21	2.13	−0.08
p-Chlorophenol	2.23	2.22	−0.01
p-Methylphenol	1.59	1.57	−0.02
p-Fluorophenol	2.14	2.10	−0.04

a) The observed values for all compounds were taken from "Tables of Electric Dipole Moments[11]" except p-fluorophenol, the value of which is due to Leonard and Sutton[12].

b) $\Delta\mu$ denotes the difference between $\mu_{obs.}$ and $\mu_{calc.}$.

TABLE V

DIPOLE MOMENTS OF o-NITROPHENOL AND ITS DERIVATIVES IN BENZENE SOLUTIONS

Compounds	$\mu_{calcd.}$(D)	$\mu_{obs.}$(D)	$\Delta\mu$(D)
o-Nitrophenol	2.77	3.16	0.39
4-Chloro-2-nitrophenol	1.95	2.35	0.40
4-Methyl-2-nitrophenol	3.07	3.49	0.42

In o-nitrophenol, therefore, the formation of intramolecular hydrogen bond causes the charge migration of the order of 0.3–0.4 D in x-direction and 0.2–0.35 D in y-direction. Such charge migration may be explained, for instance, by two main charge migrations illustrated in Fig. 2. Further studies are required, however, of other compounds similar to o-nitrophenol in order to see whether or not such charge migrations are common in the molecule having an intramolecular hydrogen bond.

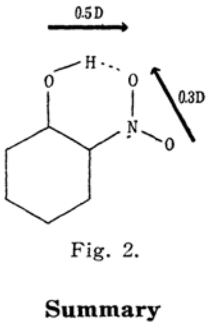

Fig. 2.

Summary

Dipole moments of o-nitrophenol, 4-chloro-2-nitrophenol, 4-methyl-2-nitrophenol, o-nitroanisole and 4-chloro-2-nitroanisole were meas-

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[10] K.B. Everard, L. Kumar and L.E. Sutton, *J. Chem. Soc.*, **1951**, 2814.

[11] L.G. Wesson, "Tables of Electric Dipole Moments", The Technology Press, M.I.T. (1948).

[12] N.J. Leonard and L.E. Sutton, *J. Am. Chem. Soc.*, **70**, 1566 (1948).

ured in benzene solutions. Their values are 3.16, 2.35, 3.49, 4.83 and 4.60 D respectively. Instead of obtaining the directions of the dipole moments of phenol and anisole, μ_x and μ_y, the two components in x- and y-directions in the molecular plane, were evaluated from the moments of their derivatives. When the dipole moments of *o*-nitrophenol, *o*-nitroanisole and their derivatives were calculated according to the vector addition using these components, the calculated moments for *o*-nitrophenol and its derivatives do not agree with the observed ones whereas fairly good agreement was found between the observed and calculated ones for *o*-nitroanisole and its derivative. The order of the discrepancy is 0.3–0.4 D in x-direction and 0.2–0.35 D in y-direction. The authors suggest that the cause of this discrepancy is due mainly to the formation of an intramolecular hydrogen bond.

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Department of Chemistry, Faculty of
Science, Nagoya University
Nagoya