mm. 2-*n*-Butyltropone (0.539 g., 83%) distilled as a colorless liquid which turned a light yellow on standing. For analysis the material was redistilled.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.4; H, 8.7. Found: C, 81.5; H, 8.7.

2-*n*-Butyltropone does not give a picrate but when dry hydrogen bromide is bubbled through an ethereal solution, there separates an oily hydrobromide which solidifies in the cold. The salt is unstable but can be crystallized from acetonitrile as a crystalline solid which, after drying in the air, liberates the original tropone.

2-*n*-Butyltropone, 0.0355 g., was hydrogenated at atmospheric pressure with 0.022 g. of 10% palladium-on-charcoal, in 5 ml. of absolute ethanol. Hydrogen absorption ceased after 3.3 mole equivalents. The ethanol was distilled from the filtered solution and the oily 2-*n*-butylcycloheptanone was converted to its 2,4-dinitrophenylhydrazone which crystallized as golden, irregular plates from ethanol; m.p. 80.0–81.5°.

Anal. Calcd. for $C_{17}H_{24}O_4N_4$: C, 58.6; H, 6.9; N, 16.1. Found: C, 58.8; H, 6.8; N, 16.0.

Tropolone Methyl Ether and Sodiomalonic Ester.—Tropolone methyl ether (0.129 g., 0.00095 mole) was added to a solution of diethyl malonate (0.152 g., 0.00095 mole) in 2 ml. of 0.475 N methanolic sodium methoxide. The resulting light orange solution was refluxed on the steam-bath for 40 min., after which time the color had turned a dark brown. Distillation of the methanol left a residue which was diluted with water and filtered. From the ether extract of the filtrate, 0.027 g. of a solid was obtained which crystallized from ethanol in fine, orange needles, m.p. 172.5–173.5°.

Anal. Calcd. for $C_{11}H_6O_4$: C, 64.7; H, 4.0. Found: C, 64.2; H, 4.2.

The ultraviolet spectrum is reported in Fig. 5.

The infrared spectra reported in Figs. 2 and 4 were obtained on a Baird Associates Infrared Spectrophotometer, with a sodium chloride prism. In the case of the solid materials the curves are composed from two spectra, one in carbon tetrachloride and the other in carbon disulfide, at 10% concentration and in 0.1-mm. cells. The liquids were measured neat in 0.025-mm. cells.

The ultraviolet spectra were measured in a Beckmann Instrument Co. Model DU ultraviolet spectrophotometer in the usual manner.

Katonah, N. Y.

Dipole Moments and Near Ultraviolet Absorption of Some Monosubstituted Benzenes — The Effect of Solvents and Hydrogen Bonding

By S. Nagakura and H. Baba

The effect of the solvent on near ultraviolet absorption spectra and dipole moments was studied with aniline, dimethylaniline, phenol and anisole. It was found that both the dipole moment and the shift of the absorption spectrum increase with the refractive index of the solvent, in the case of no specific interaction such as hydrogen bonding. The values of these two quantities are anomalously large when hydrogen bonding is formed between solute and solvent molecules. The effect of hydrogen bonding was studied in detail with phenol and aniline, by the use of mixed solvents which were made by adding a small quantity of the proton acceptor molecules to a normal solvent. The values of ΔF and ΔE due to hydrogen bonding between phenol and several proton acceptors were obtained by the near ultraviolet absorption measurement. From the present experimental results and the theory of the electron migration effect developed by Sklar and Herzfeld, it was concluded that this effect plays an important role in the solvent effect on the dipole moments and the near ultraviolet absorption spectra of phenol, anisole, aniline and dimethylaniline.

Introduction

The effects of substituents on the physical and chemical properties of the benzene molecule have been studied in terms of a resonance and an inductive effect by several workers.[1–6] It has been found that in some monosubstituted benzene molecules, such as phenol or aniline, the resonance effect is especially important in interpreting their dipole moments and near ultraviolet absorption spectra. In these molecules the near ultraviolet absorption spectra usually shift toward the side of longer wave lengths than those of benzene, and the values of the dipole moments are much different from those of the corresponding aliphatic molecules. It is often pointed out that these behaviors are principally due to the resonance effect.[1]

In the present paper, the contribution of the resonance effect to the near ultraviolet absorption spectra and the dipole moments of monosubstituted benzenes is studied by the use of the molecular orbital method developed by Sklar[2] and Herzfeld.[3] The results of these theoretical studies are used in the discussion on the effects of the solvent upon the dipole moment and the absorption spectrum, aniline, dimethylaniline, phenol and anisole being chosen as the materials for research.

Experimental

Purification of Materials.—The details for the purification of aniline, dimethylaniline, phenol, anisole and methanol have been reported previously.[7,8] Hydroquinone dimethyl ether was purified by recrystallization from methanol and ethanol (m.p. 56.3°). The solvents were purified by the method given in "Organic Solvents."[9]

Measurements and Calculations.—The determination of the dielectric constant of various solutions was made by a double beat apparatus described previously.[7] The molecular polarization at infinite dilution $P_{2\infty}$ was calculated by the Halverstadt and Kumler method.[10] From the value of $P_{2\infty}$, the dipole moment was calculated as $\mu = 0.0127 \sqrt{(P_{2\infty} - MR_D)T}$.[11]

Near ultraviolet absorption spectra of phenol, anisole, aniline and dimethylaniline in various solvents were determined with a Beckman quartz spectrophotometer model DU and with an E_7 type spectrograph made by the Institute of

(1) F. A. Matsen, This Journal, **72**, 5243 (1950).

(2) A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

(3) K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947).

(4) A. L. Sklar, *Rev. Modern Phys.*, **14**, 232 (1942).

(5) H. Hückel, *Z. Physik*, **72**, 310 (1931).

(6) W. Wheland, This Journal, **64**, 900 (1942).

(7) S. Nagakura and H. Baba, *J. Chem. Soc. Japan*, **71**, 560 (1950).

(8) H. Baba and S. Nagakura, *ibid.*, **71**, 610 (1950); **72**, 3 (1951).

(9) A. Weissberger and E. Proskauer, "Organic Solvents," Oxford Univ. Press, New York, N. Y., 1935.

(10) I. F. Halverstadt and W. D. Kumler, This Journal, **64**, 2988 (1942).

(11) Values of MR_D used for the calculation of μ are as follows: aniline, 30.6; dimethylaniline, 40.8; phenol, 28.0; anisole, 32.7; hydroquinone dimethyl ether, 39.0; methanol, 8.3.

TABLE I

DIELECTRIC CONSTANTS AND SPECIFIC VOLUMES OF VARIOUS SOLUTIONS

Wt. fraction	ϵ	v	Wt. fraction	ϵ	v
Heptane–Phenol (20.0°)			Carbon tetrachloride–Phenol (20.0°)		
0	1.943	1.4191	0	2.239	0.62710
0.00861	1.960	1.4149	0.00611	2.269	.62906
.01049	1.963	1.4142	.01438	2.310	.63163
.02166	1.983	1.4089	.01630	2.320	.63228
Heptane (10.0 g.) + dioxane (0.51 g.)–Phenol (20.0°)			Benzene–Phenol (20.0°)		
			0	2.283	1.1388
0	1.952	1.3953	0.00844	2.308	1.1365
0.01412	1.997	1.3880	.01252	2.320	1.1359
.02205	2.022	1.3834	.02539	2.363	1.1329
.04240	2.073	1.3743			
Heptane (10.0 g.) + dioxane (2.34 g.)–Phenol (20.0°)			Carbon tetrachloride–Anisole (20.0°)		
			0	2.237	0.62717
0	1.976	1.3393	0.01223	2.277	.63176
0.00849	2.005	1.3359	.01392	2.281	.63235
.01652	2.033	1.3318	.03354	2.342	.63979
.03995	2.111	1.3213			
Heptane–Anisole (20.0°)			Benzene–Anisole (20.0°)		
			0	2.284	1.1389
0	1.943	1.4187	0.00784	2.300	1.1379
0.01081	1.958	1.4142	.01594	2.314	1.1366
.01780	1.966	1.4114	.03031	2.337	1.1349
Heptane (10.0 g.) + dioxane (2.10 g.)–Anisole (20.0°)			Ether–Anisole (25.0°)		
			0	4.214	1.4130
0	1.975	1.3452	0.02449	4.230	1.4017
0.01146	1.993	1.3412	.04355	4.241	1.3924
.02686	2.017	1.3375			
.03088	2.024	1.3352	Ether–Anisole (20.0°)		
			0	4.292	1.3983
Dioxane–Anisole (20.0°)			0.02323	4.415	1.3843
0	2.227	0.96930	.03966	4.496	1.3746
0.01101	2.256	.96984	.04949	4.547	1.3750
.02441	2.283	.97034	.07647	4.674	1.3550
.03284	2.302	.97066			
			Ether–Dimethylaniline (20.0°)		
Petroleum benzine (10.0 g.) + dioxane (1.67 g.)–Anisole (20.0°)			0	4.292	1.3983
			0.02431	4.310	1.3875
0	1.950	1.3750	.04330	4.325	1.3783
0.01987	2.005	1.3666	.06370	4.332	1.3706
.04409	2.073	1.3564			
.05940	2.110	1.3501	Petroleum ether–Hydroquinone dimethyl ether (25.0°)		
Petroleum benzine (10.0 g.) + dioxane (1.67 g.)–Dimethylaniline (20.0°)			0	1.862	1.5428
			0.01412	1.890	1.5321
0	1.950	1.3750	.03499	1.932	1.5188
0.02200	1.999	1.3678	.05194	1.963	1.5079
.03930	2.030	1.3614			
.06287	2.084	1.3527	Carbon tetrachloride–Hydroquinone dimethyl ether (25.0°)		
Ether–Phenol (25.0°)			0	2.230	0.6307
0	4.214	1.4130	0.00515	2.251	.6322
0.02774	4.440	1.3944	.01571	2.298	.6357
.03959	4.541	1.3863	.02518	2.347	.6386
			.03410	2.392	.6413

Wt. fraction	ϵ	v	Wt. fraction	ϵ	v
Petroleum benzine (10.0 g.) + dioxane (0.67 g.)–Methanol (20.0°)			0.00990	2.296	1.1431
			.01932	2.319	1.1416
			.02641	2.335	1.1396
0	1.930	1.4263			
0.00535	1.969	1.4255	Dioxane–Hydroquinone dimethyl ether (25.0°)		
.01222	2.012	1.4251			
.20555	2.105	1.4236	0	2.227	0.97351
			0.01259	2.263	.97290
Benzene–Hydroquinone dimethyl ether (25.0°)			.02093	2.287	.97275
			.03802	2.342	.97204
0	2.273	1.1452			

Physical and Chemical Research, its dispersion being 12 Å./mm. at about 2800 Å. The solutions used in these absorption measurements were below 0.0006 mole/l. From the infrared absorption measurement it is evident that phenol exists only as single molecules in such low concentrations.[12]

Results.—The measured values of the dielectric constants and specific volumes of various solutions are recorded in Table I. The experimental values of the dipole moments μ and $P_{2\infty}$ obtained are given in Tables II–IV. The experimental results of near ultraviolet absorption spectra are given in Tables II–IV and in Figs. 1–4, where the molar extinction coefficient is plotted against the wave length in millimicrons. In these tables, "heptane + (dioxane)" means a mixed solvent in which a small amount of dioxane is contained in heptane. ϵ and ϵ_D are the dielectric constants for the electrostatic field and the D line of sodium, respectively. The latter is equal to the square of the refractive index for this line. λ is the wave length of the absorption maximum,[13] and $\Delta\nu$ means the wave number difference between the absorption band due to the $A_{1g} \to B_{2u}$ transition in benzene and the corresponding bands of monosubstituted benzene molecules in the same solvent.

Discussion of Results

(A) The Effect of Hydrogen Bonding on Dipole Moment and Near Ultraviolet Absorption Spectrum.—The effect of hydrogen bonding on the dipole moments of aniline and its derivatives has been studied recently by several workers[7,14,15] while its effect on the near ultraviolet absorption spectra of phenol and its derivatives has been studied only by Coggeshall[16] and the authors.[8] At this time the effect of hydrogen bonding on these two properties is simultaneously studied in detail with both phenol and aniline.

The experimental results given in Tables II and III indicate that both $|\Delta\nu|$ and apparent dipole moments of these two substances are abnormally higher in dioxane or ether than in other solvents. Such anomalies are not observed with dimethylaniline and anisole where the hydrogen atoms of the amino or the hydroxyl group of aniline or phenol are replaced by methyl groups. In addition, it is to be noticed that such anomalies are not only observed in dioxane or ether solvents but also in the mixed solvents containing a very small amount of dioxane or ether, typical proton accept-

(12) M. Tsuboi, J. Chem. Soc. Japan, **72**, 146 (1951). The authors are indebted to Mr. Tsuboi for his coöperation in discussing the possible influence of hydrogen bonding.

(13) Two main absorption maxima probably due to different vibrational transitions are observed with phenol and anisole (see Fig. 1 and 2). Of these two absorption maxima, the longer wave length one is referred to in the present paper.

(14) C. Curran and G. K. Estok, THIS JOURNAL, **72**, 4575 (1950).

(15) A. V. Few and J. W. Smith, J. Chem. Soc., 753, 2663 (1949).

(16) N. D. Coggeshall and E. M. Lang, THIS JOURNAL, **70**, 3283 (1948).

TABLE II

NEAR ULTRAVIOLET ABSORPTION SPECTRA AND DIPOLE MOMENTS OF PHENOL AND ANISOLE IN VARIOUS SOLVENTS

Solvent Name	ε (30°)	εD (20°)	λ (Å.)	Δν (cm.⁻¹)	P₂∞	μ(D)	λ (Å.)	Δν (cm.⁻¹)	P₂∞	μ(D)
			Phenol				Anisole			
Heptane	1.93	1.93	2777	−2340	66.9	1.36	2780	−2380	65.2	1.24
Heptane + (dioxane)	..	..	2805	−2710	101	1.86	2781	−2390	70.5	1.34
					101	1.86				
Dioxane	2.20	2.02	2807	−2690	92.3	1.78	2787	−2430	70.3	1.34
Carbon tetrachloride	2.22	2.13	2796	−2430	74.9	1.49	2798	−2450	66.7	1.27
Benzene	2.26	2.25	2792	−2480	77.5	1.53	2791	−2470	68.6	1.31
Ether	4.15	1.83	2807	−2680	121	2.12	2780	−2330	59.7	1.14

TABLE III

NEAR ULTRAVIOLET ABSORPTION SPECTRA AND DIPOLE MOMENTS OF ANILINE AND DIMETHYLANILINE IN VARIOUS SOLVENTS

Solvent	λ (Å.)	Δν (cm.⁻¹)	P₂∞	μ(D)	λ (Å.)	Δν (cm.⁻¹)	P₂∞	μ(D)
	Aniline				Dimethylaniline			
Heptane Petroleum	2880	−4540	77.1	1.51	2980	−5710	90.1ᵃ	1.54ᵃ
Benzine + (dioxane)	..	....	88.1	1.65	2980	−5710	96.0	1.61
Dioxane	2906	−4820	94.9ᵃ	1.78ᵃ	3000	−5900	98.0ᵃ	1.66ᵃ
Benzene	2900	−4700	79.5	1.55	3020	−6070	93.8ᵃ	1.60ᵃ
Ether	2917	−4950	90.2	1.68	2981	−5690	76.2	1.29

ᵃ S. Nagakura and H. Baba, *J. Chem. Soc. Japan*, **71**, 560 (1950). These values are measured at 30°.

TABLE IV

THE NEAR ULTRAVIOLET ABSORPTION SPECTRA AND THE DIPOLE MOMENTS OF HYDROQUINONE DIMETHYL ETHER IN VARIOUS SOLUTIONS

Solvent	Hydroquinone dimethyl ether P₂∞	μ(D)	Methanol P₂∞	μ(D)
Petroleum benzine	109.6	1.84	..	..
Petroleum benzine + (dioxane)	...	..	70.7	1.72
Carbon tetrachloride	106.3	1.80	..	..
Dioxane	104.2	1.77	83.0ᵃ	1.91ᵃ
Benzene	99.1	1.70	64.3	1.66

ᵃ H. Baba and S. Nagakura, *J. Chem. Soc. Japan*, **72**, 6 (1951).

ors—the greater part of these solvents consisting of a normal solvent, such as heptane, petroleum benzine and carbon tetrachloride. These observations seem to suggest that abnormal behaviors observed with $|\Delta\nu|$ and the apparent dipole moment of these two substances may be attributed to hydrogen bonding between solute and proton acceptor molecules as shown in the diagram

and
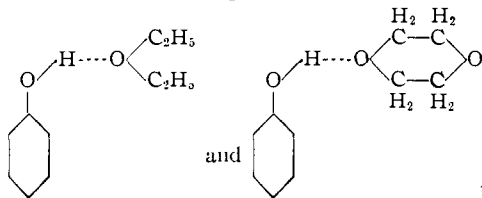
To reach a more definite conclusion in this respect, the absorption spectrum of phenol was measured in various concentration of mixed solvents. As an example, the case of the mixed solvent of dioxane and carbon tetrachloride will be discussed. When the concentration of dioxane is lower than 0.048 mole/1.[17] the absorption maximum of phenol is observed at 2796 Å. which is apparently due to free molecules of this substance. With increasing concentration of dioxane, however, the intensity of

(17) The concentration of phenol is 0.00045 mole/l. and the temperature is about 10°.

this absorption decreases and the new absorption maximum appears at 2815 Å. The intensity of the latter absorption, which seems to be due to hydrogen bridged phenol molecules, increases with increasing concentration of dioxane in the mixed solvent. At a concentration of dioxane higher than 0.15 mole/l. the former absorption maximum due to free phenol molecules disappears. This means that in such a concentration of dioxane most of phenol molecules have combined with dioxane by hydrogen bond. The same tendency was observed in other mixed solvents, such as hexane + (ether) and petroleum benzine + (dioxane). The relation between near ultraviolet absorption spectrum and hydrogen bonding may be readily seen in Fig. 1.

A similar phenomenon was also observed with aniline (Fig. 3). In the case of aniline the separation of the two absorption maxima is not as distinct as in the case of phenol.

For phenol, it is possible to obtain the values of the equilibrium constant K between free and hydrogen bridged phenol molecules from measurements of the intensity of two absorption bands. Using the value of K, the free energy difference ΔF can be calculated as $\Delta F = -RT \ln K$. From the temperature dependence of ΔF, the energy of the hydrogen bond ΔE can be obtained. The values of these quantities are given in Table V.

TABLE V

ΔF AND ΔE OF THE HYDROGEN BOND OF PHENOL IN MIXED SOLVENTS OBTAINED BY NEAR ULTRAVIOLET ABSORPTION MEASUREMENTS

Mixed solvent	ΔF, kcal./mole	ΔE, kcal./mole
Hexane + (ether)	−1.4 (at 7°)ᵃ	
Carbon tetrachloride + (dioxane)	−1.3 (at 10°)ᵃ	3.8ᵃ
Petroleum benzine + (dioxane)	−1.6 (at 23°)ᵇ	

ᵃ Measured by the E₂-type spectrograph. ᵇ Measured by the Beckman spectrophotometer model DU.

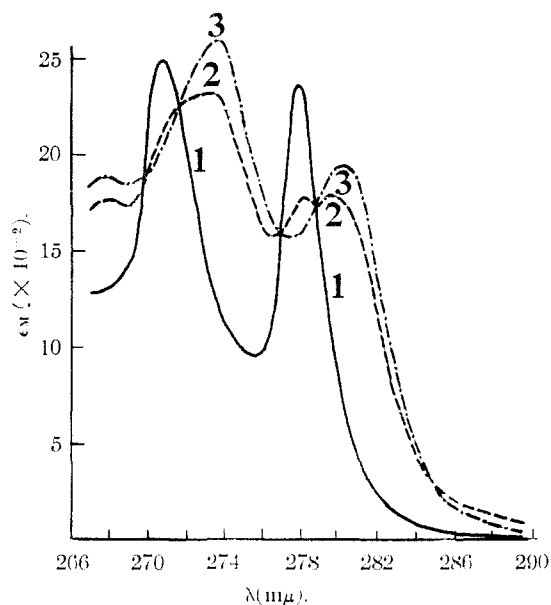By the use of the fact that O–H stretching vibration of the phenol molecule changes its frequency

Fig. 1.—The near ultraviolet absorption spectra of phenol in the mixed solvent of petroleum benzine and dioxane: curve 1, in petroleum benzine; curve 2, in the mixed solvent of petroleum benzine and dioxane (the concentration of dioxane is 0.182 mole/l.); curve 3, in the mixed solvent of petroleum benzine and dioxane (the concentration of dioxane is 0.597 mole/l.).
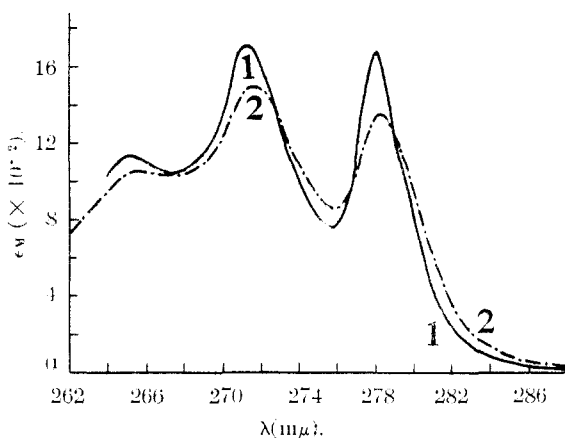

Fig. 2.—Near ultraviolet absorption spectra of anisole: curve 1, in petroleum benzine; curve 2, in the mixed solvent of petroleum benzine (10 g.) and dioxane (4.79 g.).

by hydrogen bonding, Tsuboi[12] has obtained 3.5 kcal./mole as the energy of hydrogen bonding between phenol and ether molecules in carbon tetrachloride solution. Therefore both values of ΔE obtained by the near ultraviolet and the infrared absorption measurements may be regarded as almost equal. These facts confirm the view that the above-mentioned anomalous phenomenon observed in the near ultraviolet absorption spectrum of phenol is attributable to hydrogen bonding between solute and proton acceptor molecules.

Next, we will attempt to explain the reason why $|\Delta \nu|$ and dipole moments of phenol and aniline should increase by the formation of hydrogen bond. When the electronegative oxygen atom of dioxane or ether approaches the hydrogen atom of the am-
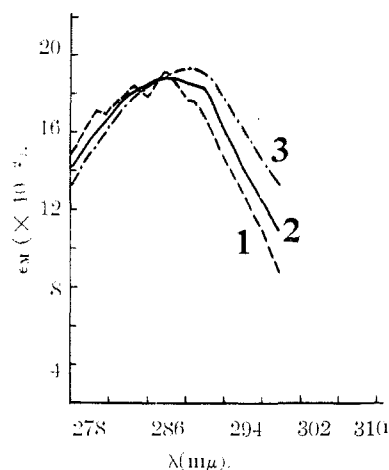

Fig. 3.—Near ultraviolet absorption spectra of aniline in various solutions: curve 1, in petroleum benzine; curve 2, in the mixed solvent of petroleum benzine (10 g.) and dioxane (1.63 g.); curve 3, in dioxane.
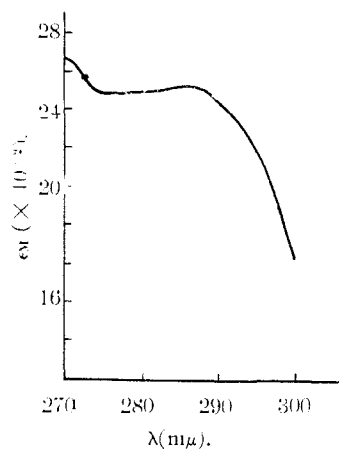

Fig. 4.—Near ultraviolet absorption spectrum of aniline in carbon tetrachloride.

ino or the hydroxyl group and a hydrogen bond forms, the valence electrons of O–H or N–H bond will presumably be displaced to a limited extent toward the oxygen or the nitrogen atom. As a result of this displacement of valence electrons, the ionization energy of the atom probably diminishes. From the molecular orbital theory described below, this seems to mean that ω in eq. (1) becomes smaller and therefore λ_j, the rate of the electron migration from the substituent into the benzene ring increases.[18] According to eqs. (3) and (4), both $|\Delta \nu|$ and μ_{mig}, the dipole moment caused by the electron migration, increases with λ_j. Furthermore, the apparent dipole moments of phenol and aniline become larger with the increment of μ_{mig}.

(18) From the standpoint of the resonance, this means that highei polar resonance structures, such as

and
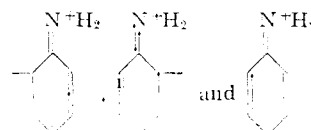
are stabilized by hydrogen bonding. This illustration based on the resonance was given by Curran to aniline and its derivatives.

Thus it seems reasonable to conclude that the foregoing anomalies in $|\Delta\nu|$ and the moments apparently due to hydrogen bonding, should be regarded as closely associated with the increase of the electron migration.

In discussing the change of the dipole moment due to hydrogen bonding, however, it may be necessary to consider some other effects than the electron migration. It is not unlikely that the change of the electron distribution in a proton acceptor and the increase in the polarity of O–H or N–H bond caused by hydrogen bonding should be a dominant factor for the increase of the apparent dipole moment. Indeed, this problem has been investigated experimentally with aniline and its derivatives by Curran[14] and other workers.[15] They compared dipole moments of aliphatic molecules with those of corresponding aromatic ones. It was concluded by Curran that some part of the increase in moment of the latter molecules resulting from hydrogen bonding may be attributable to the increased stabilization of highly polar resonance structures. Apparently the same conclusion is obtained from the experimental results on the moments of phenol and methanol in the mixed solvents.

(B) The Contribution of the Electron Migration to the Solvent Effect of the Dipole Moment and the Near Ultraviolet Absorption Spectrum in the Case of No Specific Interaction such as Hydrogen Bonding between Solute and Solvent Molecules.—
It is known from the Tables II and III that when there is no particular interaction such as hydrogen bond formation, both $|\Delta\nu|$ and apparent dipole moments of phenol, anisole, aniline and dimethylaniline become larger with ϵ_D of the solvent, with the exception of apparent moments in the dioxane solution.[19] It has been generally believed that the shift of the absorption spectra of these molecules from that of benzene is due to the electron migration effect,[1,2] while the absorption spectrum of benzene itself is little affected by the solvent.[20] Therefore it seems probable that the solvent effect on absorption spectra of monosubstituted benzenes may be principally due to the change of the electron migration by the solvent. The order of the values of $|\Delta\nu|$, viz., the degree of the solvent influence, can be explained from this point of view. According to eq. (3), derived from the molecular orbital method, this quantity $|\Delta\nu|$ should become larger with the increase in electron migration. As is generally known, the degree of electron migration increases with ϵ_D in the solution. Therefore, it is evident that $|\Delta\nu|$ should increase with the value of ϵ_D of the solvent.

On the other hand, a more complicated discussion is required to explain the solvent effect on the dipole moment. For instance, as was pointed out by Higasi[21] and Frank,[22] we cannot neglect so called

"normal solvent effect," viz., the effect of the induction in the surrounding solvent molecules by the solute dipole. The dipole moment of phenol or anisole is principally determined by the moment of O–H or O–CH$_3$ bond, because the resultant moment of the O–C (ring) bond becomes almost nil[23] by the effect of the electron migration. These bonds are supposed to lie in or near the plane of the benzene ring by the same effect.[23] Consequently the dipole moment of these substances may not make a large angle with the plane of the benzene ring. Therefore these substances should show a negative solvent effect if the induction effect alone is taken into consideration. On the contrary, the present experimental results show a definite positive solvent effect in non-polar organic solvents,[24] and the existence of "abnormal solvent effect" is clear in this case.

It has often been pointed out for aniline that the resultant dipole moment does not exist in the plane of the benzene ring. This together with the negative value of its Kerr constant was once taken as indicating a positive solvent effect for this molecule.[21,25] The electron migration effect in aniline decreases the angle (θ) between the resultant dipole moment and the C–N bond to such an extent that the dipole of this molecule should not lie in the same direction as in the alkylamine. In fact, the direction of the dipole in aniline can be calculated from the observed moments of it and of its p-derivatives, and the value of θ has been assigned 53° and 31° $\sim$ 45° by Few and Smith[26] and the authors,[27] respectively.

Although these values for θ may not be very accurate, they are still accurate enough to show definitely that the dipole is neither perpendicular to the plane of the benzene ring nor near it. Moreover, the value of θ probably becomes smaller in dimethylaniline because of the increasing electron migration effect. Therefore it seems to be erroneous to expect a positive normal solvent effect for aniline and its derivatives from the consideration of their geometrical forms.

Few and Smith concluded from their values of moment measured in carbon tetrachloride and carbon disulfide solutions that aniline has a negative solvent effect.[26] Upon examining their reasoning, one may not find it convincing, since specific interaction is observed between aniline and the two solvents. For instance, the absorption spectrum of aniline in carbon tetrachloride is anomalous as shown in Fig. 4 and precipitates are formed when these solutions are kept for a while. Therefore it seems unwise to discuss the experimental results in these two solvents. It may be necessary to consider some factors other than the induction in sur-

(19) It is observed with other substances that the value of the apparent moment is somewhat anomalous in dioxane solutions.

(20) Wave lengths of two main absorption maxima belonging to the $A_{1g} \rightarrow B_{2u}$ transition of benzene in various solutions are as follows; in heptane (petroleum benzine) 2547 Å., 2607 Å.; in dioxane 2549 Å., 2610 Å.; in carbon tetrachloride 2558 Å., 2618 Å.; in benzene 2552 Å., 2611 Å.; in ether 5249 Å., 2611 Å.

(21) K. Higasi, Sci. Papers Inst. Phys. Chem. Research (Tokyo), **28**, 284 (1937).

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(23) W. F. Anzilotti and B. C. Curran, This Journal, **65**, 607 (1943).

(24) Schupp and Mecke have measured dipole moments of phenol in such dilute solution as the effect of the association of solute molecules can be neglected. Their values are 1.32, 1.45 and 1.52 D in heptane, carbon tetrachloride and benzene solutions, respectively. So their results also support this view. K. L. Schupp and R. Mecke, Z. Elektrochem., **52**, 54 (1948).

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(27) S. Nagakura and H. Baba, J. Chem. Soc. Japan, **71**, 527 (1950).

rounding molecules by the solute dipole, in order to explain the solvent effect on the moments of these four substances. It is known from the theoretical considerations that both $|\Delta\nu|$ and μ_{mig} for these substances increase with the increment of the migration of non-bonding electrons. Therefore if we assumed that the electron migration effect plays a dominant role in the solvent effect of dipole moments as well as the near ultraviolet absorption spectra, it will be possible to explain the observed fact that the apparent moment is changed in *parallel* with $|\Delta\nu|$ by the solvent.

Further support of the above view will be found in the experimental results for hydroquinone dimethyl ether which are given in Table IV. In this substance the contributions of the electron migration by the two substituents to the apparent dipole moment have opposite directions and are compensated by each other. Consequently the contribution of the electron migration to the solvent effect on the apparent dipole moment is expected to be very small, while the normal solvent effect due to induction may be significant in this substance. From these considerations it is anticipated that the solvent effect on the dipole moment of hydroquinone dimethyl ether should be entirely different from that of anisole. This expectation is nicely fulfilled, the apparent electric moment of anisole increasing in the order heptane (petroleum benzine), carbon tetrachloride and benzene solutions, whereas the electric moment of hydroquinone dimethyl ether decreases in the same order (Table IV).

Theoretical

On the basis of the molecular orbital treatment given by Sklar[2] and Herzfeld,[3] the following formulas have been obtained for λ_j, the extent of the migration of non-bonding electrons of the substituent into the benzene ring and ΔE_{mig}, the stabilization energy due to the electron migration effect

$$\lambda_i = a_j/b = (\rho_j - T_j\omega)/(\omega - \omega_j) \quad (1)$$

$$\Delta E_{mig} = 2\sum_{j=2,3} a^2_j(\omega - \omega_j) \quad (2)$$

From eq. (1) and (2), $\Delta\nu$ and μ_{mig} can be calculated as[27]

$$\Delta\nu = \frac{1}{2hc}\left\{\frac{(\rho_1 - T_1\omega)^2}{\omega - \omega_1} - \frac{(\rho_2 - T_2\omega)^2}{\omega - \omega_2}\right\} \quad (3)[28]$$

$$\mu_{mig} = 2b^2e\left\{(\lambda_2^2 + \lambda_3^2)(a + \gamma) + \frac{\lambda_2\lambda_3}{\sqrt{2\sigma_2\sigma_3}}(3s_1 - 2)\gamma + (\lambda_2T_2 + \lambda_3T_3)a\right\} - \frac{c}{14}\left\{(b - 1)(T_0^2 + T_1^2)a - \frac{bT_1\lambda_2}{\sqrt{\sigma_1\sigma_2}}\gamma \quad (4)[28]\right.$$

where a is the distance between the substituent and the benzene ring. Other terms in eq. (1), (2), (3) and (4) are the same as those of Sklar.[2]

Using eq. (2), (3) and (4), numerical values of ΔE_{mig}, μ_{mig} and $\Delta\nu$ are calculated with phenol and aniline. The results are given in Table VI together with observed or estimated values of these quantities for purposes of comparison. As to μ_{mig} and ΔE_{mig}, the calculated values are in fairly good agreement with the estimated values, but the calculated value of $\Delta\nu$ deviates considerably from the observed. This is probably due to the fact that the approximations made in this calculation are not adequate for the excited electronic levels where the migration of non-bonding electrons of the substituent is very large.

TABLE VI
CALCULATED AND OBSERVED VALUES OF ΔE_{mig}, μ_{mig} AND $\Delta\nu$

Substance	ΔE_{mig}, e.v. Calcd.	Obsd.	μ_{mig}, D Calcd.	Obsd.	$\Delta\nu$, cm.$^{-1}$ Calcd.	Obsd.
Aniline	−0.58	−0.36[a]	1.76	1.41	−820	−4055[d]
				1.52[b]		
Phenol	− .41	− .30[a]	1.11	1.12[c]	−590	−1735[d]
				0.95		

[a] L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1940, p. 139. [b] L. G. Groves and S. Sugden, *J. Chem. Soc.*, 1992 (1937). [c] L. E. Sutton, *Proc. Roy. Soc. (London)* **A133**, 668 (1931). [d] H. Sponer and E. Teller, *Rev. Modern Phys.*, 13, 75 (1941).

(28) Equations (3) and (4) are obtained by the use of antisymmetrized molecular orbitals for A_{1g} and B_{2u} state of benzene. Equation (3) differs from the Herzfeld's equation by the factor $1/2$.