[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Stabilization of Highly Polar Resonance Structures by Hydrogen Bonding. I. Electric Moments[1]

BY COLUMBA CURRAN AND GEORGE K. ESTOK

Electrostatic interaction between hydrogen bonding solvents and organic molecules containing electron releasing groups conjugated with electron withdrawing groups results in a stabilization of the highly polar resonance structures contributing to these molecules. The increased contribution of these structures effected by this stabilization increases the polarity of the solute molecules. If the highly polar structures make a smaller contribution than the uncharged structures to the normal molecules, as is usually the case, this stabilization leads to greater electron mobility and therefore greater polarizability,[2] and to smaller electronic transition energies and therefore light absorption at longer wave lengths.[3] Other effects include alterations in the character of bonds in the conjugated chain, revealed by shifts in infrared absorption peaks. This first paper deals with changes in electric moments resulting from this solute–solvent interaction, which, regardless of its magnitude, we shall refer to as hydrogen bonding.

The compounds chosen for investigation were parasubstituted anilines. These have the advantages over the corresponding phenols of being unassociated in dilute benzene solutions and of having greater resonance polarizabilities. The only good non-polar hydrogen bonding solvent readily available is dioxane, and the increases in moment in this solvent over the values obtained in benzene solutions have been determined. We have also studied the interaction of compounds containing electron withdrawing groups with an "acceptor" non-polar solvent, *trans*-dichloroethylene. During the course of this investigation a paper by Few and Smith[4] appeared summarizing previous studies of the solvent effect on electric moments and reporting the moments of aniline in benzene and dioxane. A second article by these investigators[5] includes measurements on two of the compounds we have studied, mono-*n*-butylamine and *p*-chloroaniline.

Experimental

Preparation and Purification of Compounds.—**Mono-*n*-butylamine**, a Sharples product, was dried over magnesium sulfate, refluxed over calcium oxide and distilled through an efficient fractionating column, n^{25}D 1.3980. As the moment obtained for this compound is appreciably less than that reported by Rogers,[6] the distillate was dissolved in absolute ethanol and converted to the hydrochloride with anhydrous hydrogen chloride. The product was crystallized from an ether–alcohol mixture and the crystals were thoroughly washed with anhydrous ether to remove alcohol. They were then added, along with a small amount of water, to excess solid sodium hydroxide. The amine was decanted from this mixture, refluxed over calcium oxide and again fractionally distilled. The combined middle fractions of constant index n^{25}D 1.3980 and $d^{25}{}_4$ 0.7323 were used in making up the two most dilute benzene solutions listed in Table I. The two most concentrated solutions were prepared from the original distillate. The two samples differ in moment by not more than 0.01 debye.

***p*-Aminoacetophenone**, m. p. 106° and ***p*-nitroaniline**, m. p. 149°, Eastman Kodak Co. white label products, were used without further purification.

***p*-Chloroaniline**, a technical grade material, was crystallized first from an alcohol–water mixture and finally from hexane, m. p. 71°.

***p*-Nitrosodimethylaniline**, was recrystallized from petroleum ether, m. p. 85.5–86.0°.

***p*-Aminobenzonitrile**, an Eastman product, was kindly supplied by Dr. J. M. Vandenbelt. It was recrystallized from an alcohol-water mixture (5% alcohol), m. p. 86–86.5°.

***p*-Methoxybenzonitrile** was synthesized by Dr. F. M. Palermiti. The product was crystallized twice from an alcohol-water mixture (30% alcohol), m. p. 59.5°.

Ethyl *p*-aminobenzoate was prepared by esterifying *p*-aminobenzoic acid in the presence of hydrogen chloride. The ester was crystallized several times from an alcohol-water mixture until colorless crystals were obtained, m. p. 71°.

***p*-Methoxycinnamonitrile** was prepared by condensing anisaldehyde with cyanoacetic acid in a manner similar to the method used by Pandya and Sharma[7] for condensing *p*-dimethylaminobenzaldehyde with malonic acid. The reaction mixture was heated to 105° for forty-eight hours. The product was washed with water and extracted with ether. The ether layer was washed with 2% hydrochloric acid to remove pyridine, with 5% sodium hydroxide to remove cyanoacetic acid, and six times with 28% sodium bisulfite to remove the aldehyde. The ether was distilled off and the dark brown residue was placed in a refrigerator for a week. The product crystallized in 16% yield. Recrystallization from an alcohol-water mixture yielded white crystals melting at 64°.

Benzene, dioxane and *trans*-dichloroethylene were purified as in previous work.[8]

Measurements and Calculations.—The measurements of dielectric constants and densities have been previously described.[8] The polarizations at infinite dilution were calculated by the method of Hedestrand as modified by LeFevre and Vine.[9] Extrapolated values of the $\Delta\epsilon/wf_2$ ratios were used for those solutions for which the dielectric constant was not a linear function of the weight fraction. The electric moments in Debye units at 25° were calculated from the relation $\mu = 0.221\sqrt{P_{2\infty} - 1.05MR_D}$.

Molar refractions listed in Table II were obtained as follows: the values for mono-*n*-butylamine and *p*-chloroaniline are the solution values reported by Few and Smith.[5] The values for *p*-aminoacetophenone in benzene and dioxane, ethyl *p*-aminobenzoate in benzene, *p*-dimethylaminobenzaldehyde in benzene and *p*-nitroaniline

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[1] Presented at the 116th Meeting of the American Chemical Society. Atlantic City. September, 1949.

[2] Palermiti and Curran, THIS JOURNAL, **70**, 3257 (1948).

[3] Curran, Abstracts, 110th A. C. S. Meeting, Chicago, 1946, p. 5P.

[4] Few and Smith, *J. Chem. Soc.*, 753 (1949).

[5] Few and Smith, *ibid.*, 2663 (1949).

[6] Rogers, THIS JOURNAL, **69**, 457 (1947).

[7] Pandya and Sharma, *J. Indian Chem. Soc.*, **23**, 137 (1946).

[8] Moede and Curran, THIS JOURNAL, **71**, 852 (1949).

[9] LeFevre and Vine, *J. Chem. Soc.*, 1805 (1937).

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AT 25°

Wt. %	ϵ	d
Benzene–Mono-*n*-butylamine		
0.000	2.2730	0.87295
3.961	2.3620	.86591
5.016	2.3852	.86411
7.558	2.4402	.85961
8.773	2.4673	.85758
Dioxane–Mono-*n*-butylamine		
0.000	2.2081	1.02781
2.037	2.2645	.....
4.866	2.3383	1.00770
6.458	2.3804	1.00136
Benzene–*p*-Chloroaniline		
0.0000	2.2730	0.87289
1.0500	2.3562	.87558
1.9820	2.4302	.87794
Dioxane–*p*-Chloroaniline		
0.0000	2.2099	1.02777
0.9445	2.3183	1.02948
1.8071	2.4169	1.03101
2.7957	2.5290	1.03274
Benzene–Ethyl *p*-Aminobenzoate		
0.0000	2.2730	0.87289
1.5953	2.3958	.87627
2.5733	2.4766	.87842
3.5363	2.5577	.88051
Dioxane–Ethyl *p*-Aminobenzoate		
0.0000	2.2060	1.02777
1.2091	2.3345	1.02907
2.0222	2.4228	1.02992
3.1146	2.5416	1.03109
Benzene–*p*-Aminoacetophenone		
0.0000	2.2731	0.87283
.4525	2.3503	.....
.8812	2.4277	.87478
1.2809	2.5019	.87571
1.5094	2.5472	.87621
Dioxane–*p*-Aminoacetophenone		
0.0000	2.2081	1.02792
0.9638	2.4341	1.02904
1.3593	2.5292	1.02951
1.8472	2.6468	1.03003
Equimolar Mixture of Dioxane and *trans*-Dichloroethylene–*p*-Aminoacetophenone		
0.0000	2.1944	1.13392
0.8391	2.4050	1.13423
1.3892	2.5471	1.13437
1.7298	2.6380	1.13464
Benzene–*p*-Aminobenzonitrile		
0.0000	2.2730	0.87280
.4571	2.4268	.87380
.9254	2.5891	.87481
1.3032	2.7248	.87562
Dioxane-*p*-Aminobenzonitrile		
0.0000	2.2193	1.02807
.4430	2.4179	1.02858
.7612	2.5600	.....
.7925	2.5733	1.02902
1.1160	2.7204	1.02938
Benzene–*p*-Nitroaniline		
0.0000	2.2730	0.87289
.4107	....	.87423
.4474	2.4163	.....
.5377	2.4449	.....
.5418	....	.87464
Dioxane–*p*-Nitroaniline		
0.0000	2.2071	1.02791
0.7537	2.5338	1.02986
1.1496	2.7062	1.03089
1.4244	2.8234	1.03156
Benzene–*p*-Dimethylaminobenzaldehyde		
0.0000	2.2731	0.87283
1.0704	2.5224	.87482
1.7523	2.6815	.87612
1.9181	2.7204	.87640
trans-Dichloroethylene–*p*-Dimethylaminobenzaldehyde		
0.0000	2.1452	1.24654
0.7736	2.3922	1.24548
1.2169	2.5340	1.24486
1.3452	2.5749	1.24468
Benzene–*p*-Methoxybenzonitrile		
0.0000	2.2730	0.87285
1.0694	2.4789	.87486
1.7679	2.6136	.87611
2.2888	2.7147	.87715
Benzene–*p*-Methoxycinnamonitrile		
0.0000	2.2730	0.87280
1.0537	2.4681	.87470
1.5282	2.5552	.87562
2.3717	2.7106	.87715
trans-Dichloroethylene–*p*-Methoxycinnamonitrile		
0.0000	2.1440	1.2464
0.6414	2.3124	1.2455
0.8941	2.3773	1.2452
1.3572	2.4981	1.2446
trans-Dichloroethylene–*p*-Nitrosodimethylaniline		
0.0000	2.1412	1.24661
.3269	2.2894	.....
.6408	2.4273	1.24621
1.2481	2.6887	1.24579

in dioxane were determined in this Laboratory; the values for these compounds in other solvents were estimated. The refractions of *p*-aminobenzonitrile were estimated from the values of other compounds listed here along with the value for ethyl anisate, 50.2. The values for *p*-methoxycinnamonitrile were estimated from the refraction obtained for ethyl *p*-methoxycinnamate. The value for *p*-dimethylaminonitrosobenzene was estimated from the value obtained for *p*-dimethylaminonitrobenzene, 56.3.

TABLE II

POLARIZATIONS AND ELECTRIC MOMENTS

		$P_{2\infty}$	MR_D	μ
Mono-*n*-butylamine	benzene	60.8	24.2	1.32
	dioxane	60.8	24.1	1.32
p-Chloroaniline	benzene	221	35.8	2.99
	dioxane	271	36.4	3.36
Ethyl *p*-aminobenzoate	benzene	271	48.7	3.28
	dioxane	327	49.7	3.67
p-Aminoacetophenone	benzene	456	42.5	4.48
	dioxane	547	44.3	4.94
	(dioxane-*trans*-dichloroethylene)	532	44	4.88
p-Aminobenzonitrile	benzene	767	37.5	5.96
	dioxane	896	38.5	6.46
p-Nitroaniline	benzene	860	41	6.31
	dioxane	1014	42.9	6.88
p-Dimethylaminobenzaldehyde	(benzene)	693	51.4	5.58
	(*trans*-dichloroethylene)	703	51.8	5.63
p-Methoxybenzonitrile	(benzene)	518	38.9	4.82
p-Methoxycinnamonitrile	(benzene)	596	52	5.14
	(*trans*-dichloroethylene)	618	52.5	5.25
p-Nitrosodimethylaniline	(*trans*-dichloroethylene)	1005	55	6.80

Discussion of Results

The increase in moment from benzene to dioxane solutions for water and *n*-butyl alcohol is about 0.15 debye.[10] This increase is due to the change in electron distribution in dioxane and the increase in polarity of the H–O bonds resulting from electrostatic interaction. The H–O bond moment in water is probably as large as the H–N bond moment in substituted anilines. Any increase in moment above 0.15 resulting from electrostatic interaction between dioxane and para-substituted anilines may be attributed to the increased contribution to the solute molecules of highly polar resonance structures that are stabilized by the electrostatic interaction. It is to be expected that the greater the resonance polarizability of the substituted aniline—*i. e.*, the greater the tendency of the electron withdrawing group to acquire a negative charge—the larger will be the increase in moment from benzene to dioxane solution, provided that the moment vector of the highly polar structure is in line with the over-all moment of the compound.

The increases in moment from benzene to dioxane solution are listed in Table III. The moment of butylamine in dioxane indicates very little, if any, electrostatic interaction between solute and solvent. The values of $\Delta\mu$ for aniline and *p*-substituted anilines do not give a *direct* comparison of the relative amounts of resonance stabilization by hydrogen bonding, as (1) the H–N moment vector is probably not in the plane of the ring, and (2) the ketone and ester vectors are not in line with the vectors of the highly polar structures. The first factor is probably not very important in its effect on the relative values of $\Delta\mu$ for substituted anilines, as the projection in the plane of the ring of the resultant of the two H–N vectors is probably in line with the nitrogen-to-ring vector. The second factor is more important. Rough calculations[11] give 0.44 and 0.50 as the increases in moment that would be observed for ethyl *p*-aminobenzoate and *p*-aminoacetophenone in dioxane if the over-all moments of these compounds were in line with the moment of the highly polar structures. These values are given in parentheses in Table III and should be compared with the $\Delta\mu$ values for the other para-substituted anilines.

TABLE III

INCREASES IN MOMENT FROM BENZENE TO DIOXANE SOLUTIONS

	$\Delta\mu$
Mono-*n*-butylamine	0
Aniline[4]	0.24
p-Chloroaniline	.37
Ethyl *p*-aminobenzoate	.39 (0.44)
p-Aminoacetophenone	.46 (0.50)
p-Aminobenzonitrile	.50
p-Nitroaniline	.57

Table III reveals that the order of effect of electron withdrawing groups on resonance stabilization by electrostatic interaction is $NO_2 > CN = COR > COOR > Cl$. The difference in the $\Delta\mu$ values for aniline and *p*-chloroaniline is probably due chiefly to the increased contribution of the  structure as a result of the large C–Cl dipole. The $\Delta\mu$ value for the nitrile is somewhat larger than expected from considerations of resonance polarizabilities.[12] Otherwise, the order of $\Delta\mu$ values offers excellent evidence that the increases in moment for these compounds in dioxane are associated with increased contribution of highly polar structures in this solvent. The moments obtained for butylamine and *p*-chloroaniline are in good agreement with the values reported by Few and Smith.[5]

p-Dimethylaminobenzaldehyde and *p*-methoxycinnamonitrile show increases in moment of 0.05 and 0.11 respectively from benzene to *trans*-dichloroethylene solutions, indicating weak interaction with this latter solvent. The moment obtained for *p*-nitrosodimethylaniline in *trans*-dichloroethylene, 6.80, is less reliable because of the uncertainty in the extrapolation of the $\Delta\epsilon/wf_2$ ratios, which show an appreciable change with concentration. This value compares with a moment

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[10] "Tables of Electric Dipole Moments," Massachusetts Institute of Technology, April, 1947.

[11] The moments of ethyl benzoate and acetophenone are assumed to be in the plane of the ring (due to the large double bond character of the ring-to-carbon bond) and at angles of 74° and 55°, respectively, with the nitrogen-to-ring vector. The $^+N{=}C_6H_4{=}C{-}O^-$ moment, 29 debyes, makes an angle of 11° with this vector. As a simplification, the over-all moments of *p*-aminoacetophenone and ethyl *p*-aminobenzoate are considered to be in the plane of the ring.

[12] Palermiti and Curran, Abstracts 116th A. C. S. Meeting, Atlantic City, September, 1949, p. 72M.

of 6.76 reported by Hertel and Lebok[13] in benzene solution.

p-Aminoacetophenone has a greater molar refraction and absorbs at a longer wave length (in the ultraviolet) in a mixture of dioxane and chloroform than in either pure solvent. This is attributed to solvent interaction at both ends of the solute molecule OC_4H_8O - - - $H_2NC_6H_4CRO$ - - - $HCCl_3$. It was thought that this compound might also show a greater moment in a dioxane–*trans*-dichloroethylene mixture than in dioxane. The value obtained, however, is 0.06 debye less than in dioxane, indicating that the dichloride is a weaker "acceptor" solvent than chloroform, and that its weak interaction does not quite compensate for the decreased concentration of dioxane molecules in the vicinity of the amino group.

The moment of *p*-methoxycinnamonitrile in benzene, 5.14, shows the expected increase over the value, 4.82, observed for anisonitrile. In the light of these values, the moments reported by Weizmann[14] for *p*-dimethylaminobenzaldehyde, 5.6, and *p*-dimethylaminocinnamaldehyde, 5.4, appear somewhat anomalous.

This study of solute-solvent interaction on the electric moments of amines is being continued to determine the effect of extension of the conjugated chain.

Summary

Electric moments have been determined for mono-*n*-butylamine and some para-substituted anilines in benzene and dioxane, for *p*-methoxybenzonitrile in benzene, for *p*-methoxycinnamonitrile and *p*-dimethylaminobenzaldehyde in benzene and *trans*-dichloroethylene, and for *p*-nitrosodimethylaniline in *trans*-dichloroethylene.

The large moments observed for the substituted anilines in dioxane are interpreted as indicating increased contribution of highly polar resonance structures in this solvent resulting from the stabilization of these structures by intermolecular hydrogen bonding. A weaker solute–solvent interaction is observed in *trans*-dichloroethylene.

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[13] Hertel and Lebok, *Z. physik. Chem.*, **B47**, 315 (1940).

[14] Weizmann, *Trans. Faraday Soc.*, **36**, 329 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Concerted Displacement Reactions. V. The Mechanism of Acid-Base Catalysis in Water Solution[1]

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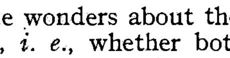
Previous studies of the displacement reactions of organic halides have demonstrated that *in benzene solution* there must always be both a nucleophilic or pushing reagent to attack carbon and an electrophilic or pulling reagent to attack halogen in the rate determining step in order to effect any reaction, regardless of whether the displacement is of the Walden inversion[2] or carbonium ion[3] type.



It has been considered by some that only nucleophilic attack is involved in the Walden inversion and only electrophilic attack in the carbonium ion mechanism. The concerted, push-pull character of the rate determining steps in benzene seemed to shed doubt on this concept of a sharp duality of mechanism.

Naturally one wonders about the generality of this conclusion, *i. e.*, whether both nucleophilic and electrophilic attack are also generally required for polar reactions *in water solution*. In most displacements in water solution, including halide displacements, water is too reactive in one or both roles relative to the other species present to permit unambiguous conclusions to be reached experimentally, but it appears that an affirmative answer can be found among reactions involving carbonyl groups, such as enolization, mutarotation and carbonyl addition. The evidence will be presented in this paper.

For the enolization of ketones it is currently accepted that there are two different mechanisms: base catalyzed and acid catalyzed.[4] In the base catalyzed mechanism only a base, or nucleophilic reagent, is involved.

$$\underset{(N)}{B^{\ominus}} + H-\underset{\begin{array}{c}|\\H\end{array}}{\overset{\begin{array}{c}R\\|\\C{=}O\\|\end{array}}{C}}-H \xrightarrow{\text{slow}} BH + \underset{\begin{array}{c}|\\H\end{array}}{\overset{\begin{array}{c}R\\|\\C{-}O^{\ominus}\\|\end{array}}{C}}-H$$

In the acid catalyzed mechanism only an acid, or electrophilic reagent, is involved.

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[1] Paper presented in the Acid–Base Symposium at the Atlantic City Meeting of the American Chemical Society, Sept. 21, 1949. For paper IV, see Swain, THIS JOURNAL, **72**, 2794 (1950).

[2] Methyl halides with pyridine, Swain and Eddy, THIS JOURNAL, **70**, 2989 (1948).

[3] Triphenylmethyl halides with methanol, Swain, *ibid.*, **70**, 1119 (1948).

[4] See, for example, Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., N. Y., 1940, pp. 229-237; Wheland, "Advanced Organic Chemistry," John Wiley and Sons, New York, N. Y., 1949, p. 255.