under reflux for 30 minutes. During this time the original deep red color had changed to dark brown. Chilling to 0° and filtering gave 0.43 g. (55%) of 5-nitroanthranilonitrile, m.p. 208–210°. Sublimation at 140° (0.05 mm.) raised the melting point to 210–211°. The reported[31] melting point for this compound is 210°.

Action of Potassium Hydroxide on 4-Methylthio-6-nitroquinazoline.—A solution of 0.5 g. of 4-methylthio-6-nitroquinazoline, 1.24 g. of potassium hydroxide, 40 ml. of water and 60 ml. of purified dioxane was stirred at room temperature for 2 hours and then evaporated under reduced pressure to a small volume. Chilling and filtering gave a brown solid which was purified by sublimation at 140° (0.02 mm.) to give 0.032 g. (9%) of 5-nitroanthranilonitrile, m.p. 210°.

Action of Chloroacetic Acid and Potassium Carbonate on 4-Mercapto-8-nitroquinazoline.—Treatment of 1 g. of 4-mercapto-8-nitroquinazoline with chloroacetic acid and potassium carbonate as described above for the 6-nitro isomer gave 0.085 g. (11%) of 3-nitroanthranilonitrile in the form of yellow needles, m.p. 125–128°. Vacuum sublimation at 100° (0.01 mm.) raised the melting point to 137–138°.

Anal. Calcd. for $C_7H_5N_3O_2$: C, 51.5; H, 3.1; N, 25.8. Found: C, 51.6; H, 3.3; N, 26.15.

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[31] H. M. A. Hartmans, *Rec. trav. chim.*, **65**, 468 (1946).

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION OF THE QUARTERMASTER RESEARCH AND ENGINEERING CENTER, NATICK, MASS.]

Base Strengths of *p*-Substituted Benzalanilines[1]

BY JULIUS WEINSTEIN AND EDWARD MCININCH

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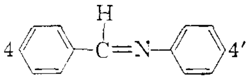
Using infrared absorbance measurements, values of K are determined at three temperatures for complex formation, through hydrogen bonding, between *p*-nitrophenol and three series of *p*-substituted benzalaniline derivatives. Values of $\Delta H°$ and $\Delta S°$ for the reaction are also calculated. For the series of compounds substituted in the aniline ring, log K values are linearly proportional to the Hammett σ-constants. For the compounds with a substituent in the benzaldehyde ring, a straight line is obtained when log K values are plotted against σ^+-constants. The correlation with σ^+-values suggests the stabilization of the hydrogen bond by resonance interaction with the *p*-substituent. In the case of the disubstituted compounds, the data are discussed in terms of an extended form of the Hammett equation.

Introduction

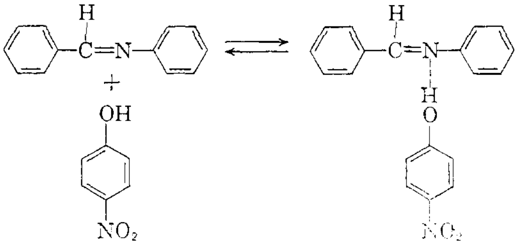
This investigation was undertaken in order to determine the effect of substituents on the base strengths of *p*-substituted benzalanilines (I).



I

Specifically, information was sought concerning the inductive and resonance effects of the substituents on the availability of the non-bonded electrons on the central nitrogen atom for hydrogen bond formation. Substituent effects may depend, for example, on whether the substituent is in the 4- or 4′-position, since structures involving resonance interaction with the nitrogen atom can be drawn with a negative charge on the nitrogen when the substituent is in the 4- but not the 4′-position.

Other workers[2-6] have shown that infrared absorption measurements of the stretching vibration band of the X-H group taking part in the intermolecular bond X—H---Y are suitable for detecting changes in the electron density at Y. Our study employed this means of detecting electron density changes at the nitrogen atom in the three series of compounds, 4- and 4′-monosubstituted and 4,4′-disubstituted benzalanilines. *p*-Nitrophenol served as the proton donor. The solvent was carbon tetrachloride. Formation of the O—H---N bond produced a decrease in the intensity of the free O-H infrared absorption band of the proton donor. Measurements of the absorbance of the free O-H band, therefore, permitted the calculation of K for the equilibrium



In addition, values of $\Delta H°$ and $\Delta S°$ for the reaction were calculated from the dependence of K upon the temperature.

Experimental

***p*-Substituted Benzalanilines.**—The compounds were prepared for the most part by heating together equimolar amounts of the appropriate benzaldehyde and aniline derivatives for 1 hour on a steam-bath. The procedure of Miller and Plöchl[7] was used to prepare N-benzylidine-*p*-nitroaniline. N-*p*-Chlorobenzylidine-*p*-chloroaniline was prepared by refluxing an ethanolic solution of equimolar quantities of the reactants for 1 hour. The product precipitated on cooling.

Compounds were purified by recrystallization from ethanol or another suitable solvent. The products were characterized by comparison of their melting points with reported values. Two new compounds were prepared, N-*p*-bromobenzilidineaniline (m.p. 72.5–73.0°: *Anal.* Calcd. for $C_{13}H_{10}NBr$: C, 60.02; H, 3.88; N, 5.38; Br, 30.72. Found: C, 59.90; H, 3.76; N, 5.33; Br, 30.56) and N-*p*-dimethylaminobenzilidine-*p*-chloroaniline (m.p. 149.5–150.5°: *Anal.* Calcd. for $C_{15}H_{15}N_2Cl$: C, 69.62; H, 5.84; N, 10.83; Cl, 13.70. Found: C, 69.42; H, 5.70; N, 10.78; Cl, 13.59).

Method and Calculations.—The concentration of *p*-nitrophenol in CCl_4 was always 0.001 M. The concentration of the benzaldehyde derivative was usually 0.008 M. In

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[1] Presented at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

[2] M. Tsuboi, *J. Chem. Soc. Japan*, **72**, 146 (1951); *Bull. Chem. Soc. Japan*, **25**, 60 (1952).

[3] Y. Sato and S. Nagakura, *Sci. of Light*, **4**, 120 (1955).

[4] H. Baba and S. Nagakura, *J. Chem. Soc. Japan*, **71**, 613 (1950).

[5] S. Nagakura and H. Baba, THIS JOURNAL, **74**, 5693 (1952).

[6] S. Mizushima, M. Tsuboi, T. Shimanouchi and Y. Tsuda, *Spectrochim. Acta*, **7**, 100 (1955).

[7] W. v. Miller and J. Plöchl, *Ber.*, **25**, 2020 (1892).

several cases, due to low solubility, it was necessary to use a more dilute solution of the benzalaniline. An excess of Schiff base to *p*-nitrophenol was maintained in order to decrease the possibility of more than one mole of *p*-nitrophenol bonding to the benzalaniline. At the concentration of *p*-nitrophenol used no absorption band attributable to associated phenol was observed in the 3 μ region of the infrared spectrum. It was not necessary, therefore, to take into consideration an additional equilibrium between free and associated phenol.

The absorbance of λ_{max} of the free OH infrared absorption band at 2.77 μ in the spectrum of *p*-nitrophenol was used to calculate the equilibrium concentration of uncomplexed phenol. It was found that the absorption at 2.77 μ of *p*-nitrophenol in CCl_4 obeyed Beer's law over the range of uncomplexed phenol concentrations in the equilibrium measurements. The decrease in intensity of the 2.77 μ band on complex formation was accompanied by the appearance of a new band at longer wave lengths due to associated OH. This new band did not overlap with the 2.77 μ band and, therefore, did not interfere with the absorbance measurements.

The possibility of *p*-nitrophenol hydrogen bonding with the substituents was investigated. With the possible exception of the nitro group when in the 4′-position, the substituents did not hydrogen bond with the proton donor under the experimental conditions employed. Solutions of either dimethylaniline or anisole at the same concentration employed for measurement of the Schiff bases did not show a significant decrease in the intensity of the 2.77 μ band of *p*-nitrophenol.

Values of $\Delta H°$ were calculated from the slopes of the least square straight lines fitting the plots of log *K versus* $1/T$. Values of $\Delta S°$ were calculated from the relationship $\Delta F° = \Delta H° - T\Delta S°$.

Infrared Measurements.—A Beckman IR-3 spectrophotometer equipped with LiF optics was used. Solutions were measured in a 2.0-cm. cell against a reference of pure carbon tetrachloride in the same cell. The temperature of the samples was controlled by circulating water or oil from a constant temperature bath through the jacketed cell compartment. Temperature measurements were made by a thermocouple attached to the cell.

Results and Discussion

Monosubstitued Benzalanilines.—The effect of *p*-substituents on the electron density at the nitrogen atom as reflected by changes in the absorbance at 2.77 μ is presented in Fig. 1 for the series of 4-substituted derivatives. Similar results are also observed for the 4′-series. Tables I and II give the values of *K* obtained for the 4- and 4′-substituted benzalanilines, respectively. In each series there is a decrease in hydrogen bonding power in going from $N(CH_3)_2$ to NO_2. This decrease is accompanied by a decrease in the electron-repelling power of the substituents. It will be noted that the values of *K* are larger when the substituent is in the 4-position. In addition, the range of values of *K* for the 4-substituted compounds is approximately twice that found for the 4′-series.

TABLE I

VALUES OF *K* FOR THE 4-SUBSTITUTED SERIES

Substituent	σ^{+8}	$K \times 10^{-1}$ 18.0°	27.5°	48.0°
$N(CH_3)_2$	-1.79^9	40	28	13
OCH_3	−0.764	13	8.8	4.5
CH_3	− .306	8.4	6.1	3.1
H	0	5.9	3.9	1.9
Cl	0.112	4.2	2.9	1.4
Br	.148	3.8	2.5	1.3
NO_2	.777	2.3	1.2	0.66

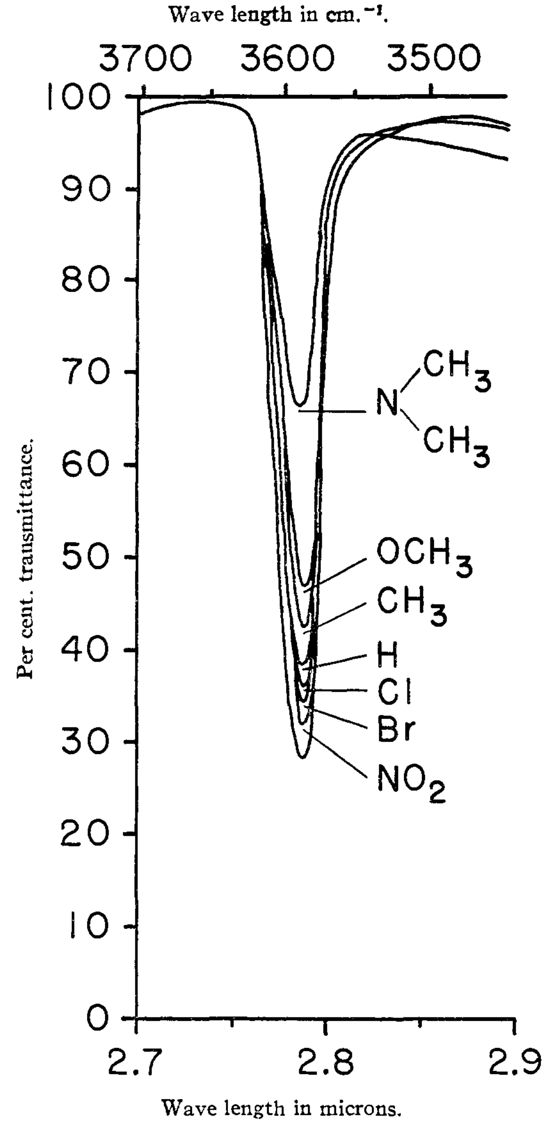

Fig. 1.—Infrared absorption curves of *p*-nitrophenol in the solutions: carbon tetrachloride + *p*-nitrophenol, 0.001 *M*, + 4-substituted benzalaniline, 0.008 *M*.

In the case of the 4′-series the change in the electron density at the nitrogen atom is linearly proportional to the Hammett σ-values.[11] When log *K* values are plotted against σ-constants the values of the reaction constant (ρ) for the least square lines at 18.0, 27.5 and 48.0° are −0.925, −0.934, −0.958

TABLE II

VALUES OF *K* FOR THE 4′-SUBSTITUTED SERIES

Substituent	σ^{10}	$K \times 10^{-1}$ 18.0°	27.5°	48.0°
$N(CH_3)_2$	−0.600	19	14	7.3
OCH_3	− .268	9.4	6.3	3.5
CH_3	− .170	8.0	6.1	3.1
H	0	5.9	3.9	1.9
Cl	0.227	3.2	2.5	1.1
Br	.232	3.2	2.1	1.3
NO_2	.778	2.2	1.3	0.56

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(8) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

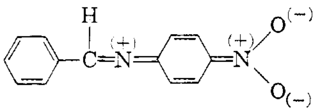
(9) N. C. Deno and W. L. Evans, THIS JOURNAL, **79**, 5804 (1957).

(10) H. H. Jaffé, *Chem. Revs.*, **53**, 222 (1953).

(11) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 184.

and the values of the correlation coefficients (*r*) are 0.997, 0.994 and 0.996. The correlations are considered excellent on the arbitrary scale proposed by Jaffé.[12] The base strengths of the compounds in the 4′-series, therefore, are influenced by the inductive and resonance polar effects of the substituents.[13]

In the case of the 4′-nitro group, however, the values of *K* are too large. This may be due to an enhanced basicity of the nitro group when in this position, because of the contribution of the following resonance form to the ground state structure. As a result, the nitro group may be hydrogen bonded with *p*-nitrophenol.

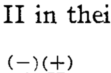


For the 4-substituted series straight lines are obtained when the log *K* values are plotted against the electrophilic substituent constants, σ^+. The correlation coefficients for the lines at 18.0, 27.5 and 48.0° are 0.985, 0.991 and 0.990, respectively, and the values of ρ are -0.493, -0.543 and -0.511, respectively. The slopes of the lines on which the compounds in the 4-series fall are not as steep as those observed for the 4′-substituted compounds. Apparently polar effects are transmitted to the nitrogen atom more readily when a group is in the 4′-position. This may be attributed to the shorter path length involved. The correlation of the 4-series with σ^+-constants and the increase in values of the equilibrium constants when substituents are in the 4-position indicate that in addition to the inductive and resonance polar effects of the substituents another factor must be taken into consideration.

Recent quantum mechanical treatments[14,15] of the hydrogen bond based on a one-dimensional model describe the bond by means of the resonance structures I, II and III. Lippincott and Schroeder,[16] neglecting II in their model, also attain considerable success in explaining properties of the hydrogen bond. In these treatments the resonance structure III is considered to make a significant contribution to the bond energy. In the 4-substituted benzalanilines the contribution of structures corresponding to III may be enhanced by the additional form V, involving resonance interaction with the substituent, as shown in IV ⟷ V.

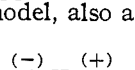
-A-H :B

I



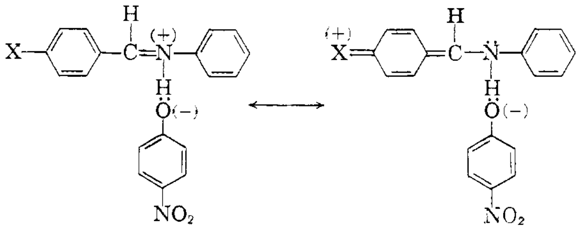
$$\overset{(-)}{\text{-A}}\!:\!\overset{(+)}{\text{H}}\ :\text{B}$$

II



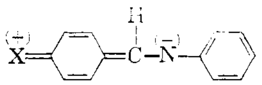
$$\overset{(-)}{\text{—A}}\!:\!\text{H—}\overset{(+)}{\text{B}}$$

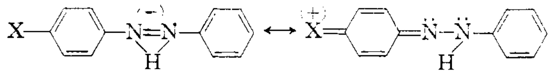
III



IV ⟷ V

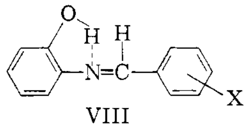
An alternate explanation is that the basicity of the nitrogen atom is increased by contributions of a resonance form of the following type to the structure in the ground state. However, this resonance structure is usually considered to be more important in the excited state.[17,18] Further, a correlation with σ^+-constants would be expected to apply only to systems involving resonance interaction of a substituent with an electron deficient center, such as the nitrogen atom in structure IV.[19,20] Yeh and Jaffé[21] attribute the correlation of *pK*'s with σ^+-constants for two series of substituted azobenzenes to resonance in the conjugate acids (*cf.* structures VI → VII).





VI ⟷ VII

In a recent paper, Baker and Shulgin[22] report a study of the effect of *o*-, *m*- and *p*-substituents on the intramolecular hydrogen bonding in *o*-hydroxy Schiff bases of the type represented by structure VIII. The displacement in the infrared spectrum of the vibration of the associated OH group ($\Delta\nu_{OH}$, measured with respect to a hydrogen substituent) is taken as a measure of the strength of the hydrogen bond. In a plot of $\Delta\nu_{OH}$ for the *m*- and *p*-substituted compounds *versus* σ-values, the point for the *p*-NO_2 group falls off the line. When the data of Baker and Shulgin are replotted[23] using σ^+-parameters in place of σ-values for the *p*-substituted series, excellent correlations are obtained ($r = 0.993$ for the *para* and 0.994 for the *meta* compounds). For the *p*-substituted series resonance similar to structures IV⟷V may contribute to the structure of the intramolecular hydrogen bond. The *m*- and *p*-substituted series each fall on curves of different slopes ($\rho = 0.0621$ for the *para* and 0.0311 for the *meta* series). Hine,[24] in a recent theoretical analysis of the Hammett equation, con-



VIII

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[12] See ref. 10, p. 236.

[13] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., p. 570.

[14] C. A. Coulson and V. Danielsson, *Ark. Fys.*, **8**, 239 (1954).

[15] P. C. McKinney and G. M. Barrow, *J. Chem. Phys.*, **31**, 294 (1959).

[16] E. R. Lippincott and R. Schroeder, *ibid.*, **23**, 1099 (1955).

[17] E. R. Blout and M. Fields, THIS JOURNAL, **70**, 189 (1948).

[18] L. N. Ferguson and T. C. Goodwin, *ibid.*, **71**, 633 (1949).

[19] H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957).

[20] H. C. Brown in "Steric Effects in Conjugated Systems," G. W. Gray, Ed., Academic Press, Inc., New York, N. Y., 1958, p. 100.

[21] Si Jung Yeh and H. H. Jaffé, THIS JOURNAL, **81**, 3279 (1959).

[22] A. W. Baker and A. T. Shulgin, *ibid.*, **81**, 1523 (1959).

[23] For this plot the σ^+-constants used for $N(CH_3)_2$, OH and F are those given in ref. 9 evaluated from the reaction $ArSi(CH_3)_3 + H^+$. The σ^+-values used for the other substituents are given in ref. 8. The σ_m-constants are those used by Baker and Shulgin.

[24] J. Hine, THIS JOURNAL, **81**, 1126 (1959).

TABLE III

VALUES OF $\Delta H°$, $\Delta S°$ AND $\Delta F°$ FOR THE MONOSUBSTITUTED COMPOUNDS

4-Series						4′-Series					
	$\Delta F°^a$						$\Delta F°^a$				
Substituent	18.0°	27.5°	48.0°	$\Delta H°^a$	$\Delta S°^b$	Substituent	18.0°	27.5°	48.0°	$\Delta H°^a$	$\Delta S°^b$
$N(CH_3)_2$	−3.5	−3.4	−3.1	−7.0	−12	$N(CH_3)_2$	−3.0	−3.0	−2.7	−5.9	−10
OCH_3	−2.8	−2.7	−2.4	−6.6	−13	OCH_3	−2.6	−2.5	−2.3	−6.0	−12
CH_3	−2.6	−2.7	−2.2	−6.0	−12	CH_3	−2.5	−2.4	−2.2	−6.0	−12
H	−2.4	−2.2	−1.9	−7.1	−16	H	−2.4	−2.2	−1.9	−7.1	−16
Cl	−2.2	−2.0	−1.7	−6.5	−15	Cl	−2.0	−1.9	−1.5	−6.7	−16
Br	−2.1	−1.9	−1.6	−6.6	−15	Br	−2.0	−1.8	−1.6	−5.5	−12
NO_2	−1.8	−1.4	−1.2	−7.2	−19	NO_2	−1.8	−1.6	−1.1	[c]	[c]

[a] Kcal./mole. [b] e.u. [c] Not determined.

cludes that ρ cannot be expected to be the same for *m*- and *p*-substituents. This conclusion is also borne out statistically.[25] The unsubstituted compound seems to fit in best with the *m*-substituted groups. Jaffé[25] also finds this to be the case in some of the instances in which differences are observed in the fit of *m*- and *p*-substituted compounds to the Hammett equation.

In Table III thermodynamic constants for the monosubstituted compounds are listed. While the values of $\Delta H°$ fall within the range normally observed for the energy of hydrogen bonds,[26] they do not show the trend anticipated. One would expect a decrease in $\Delta H°$ values in going from the dimethylamino to the nitro derivative corresponding to the observed trend in values of the equilibrium constants. It is found, however, that the $\Delta H°$ values for the electron attracting groups are as large as those observed for the electron-repelling substituents. In the case of the 4-nitro and 4′-chloro derivatives, larger values of $\Delta H°$ are observed than for the dimethylamino substituted compounds in each series. Also surprising is the fact that the values of $\Delta S°$ are not constant in each series, but tend to increase in going to the more electron-attracting substituents. This observation cannot be explained on the basis of a steric effect, since substituents in the *p*-positions cannot hinder the approach of *p*-nitrophenol to the central nitrogen atom. Ross and co-workers,[27] in a study of charge-transfer complex formation between 2,4-dinitrochlorobenzene and several substituted anilines, report similar findings with regard to the $\Delta H°$ and $\Delta S°$ values for the reactions. Perhaps the results of the present investigation are being influenced to some extent by the formation of charge-transfer type intermolecular bonds.

Disubstituted Benzalanilines.—The equilibrium constants observed for the disubstituted compounds are given in Table IV. The range of the *K*-values suggests the applicability of the extended Hammett equation

$$\log K = \rho_1\sigma^+ + \rho_2\sigma$$

Here ρ_1 and ρ_2 are the reaction constants found for the 4- and 4′-monosubstituted series, respectively, and σ^+ and σ are the substituent constants for groups in the 4- and 4′-positions, respectively. Log *K* values are plotted against $\rho_1\sigma^+ + \rho_2\sigma$. Values of ρ at 18.0, 27.5 and 48.0° are 0.910, 0.927, 1.01 and correlation coefficients of the curves are 0.996, 0.994 and 0.995. The excellent fit of the data to the above equation shows that the base strength is an additive function of the transmission of the polar effects of the *p*-substituents to the nitrogen atom.

TABLE IV

VALUES OF *K* FOR THE DISUBSTITUTED SERIES

Substituents		$K \times 10^{-1}$		
4-	4′-	18.0°	27.5°	48.0°
$N(CH_3)_2$	$N(CH_3)_2$	10.0	8.0	5.3
$N(CH_3)_2$	Cl	[a]	1.5	0.95
OCH_3	OCH_3	1.8	1.2	.64
OCH_3	CH_3	1.5	1.2	.52
NO_2	$N(CH_3)_2$	0.59	0.36	.21
H	H	.59	.39	.19
Cl	Cl	.28	.15	.085

[a] Not measured because of low solubility.

Thermodynamic constants are given in Table V. As observed for the monosubstituted compounds, values of $\Delta H°$ and $\Delta S°$ vary and tend to increase as the values of the equilibrium constant decrease. The variations in $\Delta S°$ indicate that in addition to potential energy changes, the equilibrium constants are being influenced by some other factor or factors which are not apparent at the present time.

TABLE V

VALUES FOF $\Delta H°$, $\Delta S°$ AND $\Delta F°$ FOR THE DISUBSTITUTED COMPOUNDS

Substituents		ΔF^0, kcal./mole			ΔH^0, kcal./mole	ΔS^0, e.u.
4-	4′-	18°	27.5°	48.0°		
$N(CH_3)_2$	$N(CH_3)_2$	−4.0	−4.0	−4.0	−4.1	− 0.28
$N(CH_3)_2$	Cl	[a]	−3.0	−2.9	[a]	[a]
OCH_3	OCH_3	−3.0	−2.8	−2.6	−6.3	−11
OCH_3	CH_3	−2.9	−2.9	−2.5	−6.8	−13
NO_2	$N(CH_3)_2$	−2.4	−2.1	−1.9	−6.2	−13
H	H	−2.4	−2.2	−1.9	−7.1	−16
Cl	Cl	−1.9	−1.6	−1.4	−7.0	−18

[a] Not determined because of low solubility at 18.0°.

Acknowledgments.—The authors are indebted to Dr. J. D. Margerum for some valuable discussions, to Mr. J. A. Sousa who prepared some of the compounds, and to Mr. C. DiPietro for the chemical analyses.

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[25] H. H. Jaffé, THIS JOURNAL, **81**, 3020 (1959).

[26] L. N. Ferguson, "Electron Structures of Organic Molecules," Prentice-Hall, Inc., New York, N. Y., 1952, p. 57.

[27] S. D. Ross, M. Bassin and I. Kuntz, THIS JOURNAL, **76**, 4176 (1954).