and had a density of 0.81 g./ml. at 22°. Calculating for lithium isobutoxide content, we obtained a solubility value of 1.3 wt. % at 22°.

Lithium *n*-butoxide, unlike the isobutoxide, did not crystallize from its *n*-butyl alcohol solution on cooling to room temperature. Its solubility in *n*-butyl alcohol was subsequently found to be greater than 5 moles/l. Lithium methoxide, ethoxide, and *n*-propoxide were also found to be quite soluble in their respective alcohols at room temperature.

C. Solubility of Lithium *n*-Butoxide in *n*-Heptane Solutions Containing *n*-Butyllithium.—The following experimental scheme was employed. About 100 to 200 ml. of a certain required molarity of *n*-butyllithium solution in pure grade *n*-heptane was accurately measured out and transferred to a three-necked, round-bottom, argon-swept flask equipped with a mechanical stirrer, reflux condenser (argon inlet tube at top), and a 10-ml. buret fitted (at its lower end) with a rubber stopper and its upper end with an argon-inlet tube. The required amount of Fisher certified reagent *n*-butyl alcohol needed to convert half the *n*-butyllithium to lithium *n*-butoxide was then added slowly to the stirred, cooled *n*-butyllithium solution. The mixture was allowed to stir for about a 0.5-hr. period and was then allowed to stand overnight. Precipitation was complete by this time. A sufficiently large sample (about 35 ml.) of the clear solution was then filtered off into a graduated dropping funnel, through a sintered-glass filter tube (Ace Glass Co., E porosity), to obtain analyses for *n*-butyllithium[2] and total base concentrations. The remainder of the mixture in the flask was then transferred to a graduated dropping funnel under argon to determine the total volume of salts and solution. Initial *n*-butyllithium concentrations were 2.54, 1.05, 0.78, 0.51, and 0.38 *M*. In all cases addition of one-half of the equivalent amount of *n*-butanol resulted in the formation of a precipitate.

The following amounts of reagents were employed in each of five determinations: (1) 87.5 ml. of 2.90 *M* *n*-butyllithium solution diluted to 100 ml. with *n*-heptane and 11.60 ml. (9.4 g., 0.127 mole) of *n*-butyl alcohol (initial *n*-BuLi concentration = 2.54 *M*); (2) 100 ml. of 1.05 *M* *n*-butyllithium solution in pure *n*-heptane and 4.80 ml. (3.89 g., 0.0525 mole) of *n*-butyl alcohol, (initial *n*-BuLi concentration = 1.03 *M*); (3) 26.8 ml. of 2.90 *M* *n*-butyllithium solution diluted to 100 ml. with *n*-heptane, and 3.65 ml. (2.96 g. 0.04 mole) of *n*-butyl alcohol (initial *n*-BuLi concentration = 0.78 *M*); (4) 17.5 ml. of 2.90 *M* *n*-butyllithium solution diluted to 100 ml. with *n*-heptane, and 2.32 ml. (1.88 g., 0.025 mole) of *n*-butyl alcohol (initial *n*-BuLi concentration = 0.51 *M*); (5) 13.0 ml. of 2.90 *M* *n*-butyllithium solution diluted to 100 ml. with *n*-heptane, and 1.73 ml. (1.4 g., 0.019 mole) of *n*-butyl alcohol (initial *n*-butyllithium concentration = 0.38 *M*).

In addition to the above, one run was made in which an equivalent amount of *n*-butyl alcohol was added to an *n*-butyllithium solution. *n*-Butyl alcohol (8.12 ml., 6.59 g., 0.089 mole) was added to 30.6 ml. of *n*-butyllithium in *n*-heptane diluted to 100 ml. with pure *n*-heptane.

Structure–Property Relations for Some 4-Substituted 2-Nitroanilines[1]

JAMES O. SCHRECK, C. KINNEY HANCOCK,[2] AND RICHARD M. HEDGES

Department of Chemistry, Texas A & M University, College Station, Texas

Received June 8, 1965

The pK_A values at 25° of 12 4-substituted 2-nitroanilines in perchloric acid have been measured and quantitatively related to Hammett σ values. The value of the reaction constant for the series does not conform with Jaffé's assumption for a constant *ortho* effect. The variation is discussed. The electronic spectral data correlate with σ and a fair correlation was obtained between ν_B and ν_A. The polarographic reduction half-wave potentials for the series at the dropping mercury electrode have been obtained. It appears that no $\rho\sigma$ relationship exists. The attempted polarographic oxidation of the series using a rotating platinum electrode was unsuccessful. The N–H fundamental frequencies and intensities have been determined for 10 members of the series. The asymmetric frequencies, symmetric frequencies, band intensities, and half-band widths individually correlate with σ. The Hückel molecular orbital treatment is applied to four members of the series and linear relationships exist between π-electron densities and σ and between β coefficients and σ.

The Hammett equation has been successfully employed in deriving quantitative relationships between structure and chemical reactivity.[3a] Also, certain physical properties, *e.g.*, half-wave potentials from polarographic reactions,[3b] electronic spectral excitations,[4–6] infrared absorption frequencies,[3c] and electron densities calculated by molecular orbital theory,[3d] have been correlated with Hammett substituent constants.

Essentially, this article is a study of the applicability of the Hammett equation to acidity, electronic spectral excitations, polarographic reduction potentials, infrared N–H absorption frequencies and band intensities, and electron densities calculated by HMO theory of a series of 4-substituted 2-nitroanilines.

The 4-substituted 2-nitroanilines provide an excellent series for such a study. The nitro group ensures that the electronic spectrum of importance to this study will appear in the easily accessible visible or near-ultraviolet region. The presence of the nitro group *ortho* to the amino group is advantageous in that it chelates with the amino group, thereby preventing molecular association, and it is sufficiently removed from the 4-substituent that no steric interaction can take place. Furthermore, the presence of the nitro group is convenient for the determination of polarographic half-wave reduction potentials. Finally, the amino group provides for a suitable study of the substituent effect on N–H stretching frequencies.

Results and Discussion

The Correlation of the Acidity and Electronic Spectra of 4-Substituted 2-Nitroanilines with Substituent Constants.—It has been previously shown for 2,4-dinitrophenylhydrazones[4,5] that differences ($\Delta\nu$) between wave numbers of visible spectra of neutral and alkaline solutions are quantitatively related to Hammett[7a] and Taft[8] substituent constants. More recently, it has

---

[1] Abstracted in part from the Ph.D. Dissertation of J. O. S., Texas A & M University, Aug. 1964.

[2] To whom inquiries should be sent.

[3] H. H. Jaffé, *Chem. Rev.*, **53** (1953): (a) Tables 1 and 2, pp. 198 ff; (b) Table 3A, p. 214; (c) Table 3B, p. 214; (d) p. 227; (e) p. 253; (f) p. 222; (g) pp. 246–248; (h) Table 1, reaction no. 26a, p. 200.

[4] L. A. Jones and C. K. Hancock, *J. Org. Chem.*, **25**, 226 (1960).

[5] L. E. Scoggins and C. K. Hancock, *ibid.*, **26**, 3490 (1961).

[6] M. Rapoport, C. K. Hancock, and E. A. Meyers, *J. Am. Chem. Soc.*, **83**, 3489 (1961).

[7] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940: (a) Chapter 7; (b) p. 267.

[8] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619.

Table I

Acidity and Spectral Data for 4-Substituted 2-Nitroanilines in Perchloric Acid

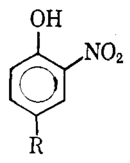
Compd.	4-Substituent	$pK_A{}^a$	$\lambda^b{}_B$	$\nu_B{}^c \times 10^{-4}$	$\epsilon_B{}^d \times 10^{-3}$	$\lambda_A{}^e$	$\nu_A{}^f \times 10^{-4}$	$\epsilon_A{}^g \times 10^{-3}$	$\Delta\nu^h \times 10^{-4}$	$\sigma_p{}^i$	$\sigma_p{}^{+j}$
2	OC_4H_9	+0.74 (+0.78)	450	2.22	4.45	276	3.62	5.10	−1.40	−0.320	...
3	OCH_3	+0.77 (+0.73)	449	2.23	4.66	274	3.65	5.11	−1.42	−0.268	−0.778
4	CH_3	+0.43 (+0.39)	429	2.33	4.18	272	3.68	6.73	−1.35	−0.170	−0.311
5	H	−0.29^k (−0.29)	415	2.41	4.42	256	3.91	7.07	−1.50	0.000	0.000
6	F	−0.44 (−0.34)	425	2.35	4.78	261	3.83	6.70	−1.48	0.062	−0.073
7	C_6H_5	−0.76 (−0.88)	437	2.29	3.96	255	3.92	22.4	−1.63	0.009	−0.179
8	Cl	−1.03^l (−1.03)	423	2.36	4.59	263	3.80	6.49	−1.46	0.227	0.114
9	Br	−1.05 (−1.10)	427	2.34	4.38	267	3.74	5.82	−1.40	0.232	0.150
10	CF_3	−2.25 (−2.31)	398	2.51	5.34	255	3.92	6.59	−1.41	0.551	0.612
11	CO_2CH_3	−2.61 (−2.57)	409	2.44	4.55	261	3.83	7.19	−1.39	0.636	...
13	$COCH_3$	−2.85	399	2.51	2.79	230	4.35	12.3	−1.84	0.874	...
14	NO_2	−4.33^m	345^m	2.90	14.3	234^m	4.27	17.6	−1.37	1.27	...

[a] The pK_A values in parentheses were determined in hydrochloric acid solution. All pK_A values include a correction for the activity of the anion. A minimum of four determinations was made for each pK_A; average deviation from the mean was ±0.025. [b] λ_B (mμ) = λ_{max}^{NaOH}. [c] ν_B (cm.$^{-1}$) = $(1/\lambda_B \times 10^7)$. [d] ϵ_B = extinction coefficient in alkaline solution. [e] λ_A (mμ) = $\lambda_{max}^{HClO_4}$. [f] ν_A (cm.$^{-1}$) = $(1/\lambda_A \times 10^7)$. [g] ϵ_A = extinction coefficient in acid solution. [h] $\Delta\nu$ (cm.$^{-1}$) = $(\nu_B - \nu_A)$. [i] Except as noted, all σ values are from Jaffé.[3f] [j] Ref. 16. [k] Ref. 31, $pK_A = -0.29$ (apparent). [l] Ref. 31, $pK_A = -1.03$. [m] T. G. Bonner and J. C. Lockhart [*J. Chem. Soc.*, 2840 (1957)] report $pK_A = -4.36$, λ_B = 348 mμ, and λ_A = 235 mμ. Ref. 31, $pK_A = -4.55$.

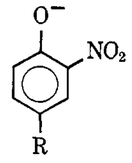
been observed that certain aspects of the electronic spectra of 4-substituted 2-nitrophenols,[6] 5-substituted 2-nitrophenols,[9] and 4-substituted 2-chlorophenols,[10] conform to a σρ treatment. These observations support the theory that substituents which affect chemical reactivity similarly affect the electronic spectra. Furthermore, this property, normally considered as physical, behaves as though it has some of the characteristics of a chemical reaction.

In view of the successful spectra–structure correlations obtained by these workers, and especially those of Rapoport,[6] it seemed desirable to expand the scope of the study. One purpose of this article is to observe and comment upon the results produced by changing the series from 4-substituted 2-nitrophenols to 4-substituted 2-nitroanilines, while maintaining all other conditions as similar as possible to those of Rapoport. Accordingly, the pK_A values in perchloric acid and absorption spectra of a series of 4-substituted 2-nitroanilines have been measured. The experimental data are shown in Table I. All absorption bands recorded are the maxima and the pK_A values reported are for the conjugate acids of the substituted anilines. The pK_A values in parentheses in Table I were determined in hydrochloric acid solution.

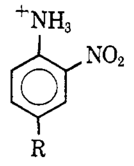
Rapoport[6] observed a bathochromic shift in basic media for I → II. For I, which exists in acidic media, there is intramolecular hydrogen bonding and resonance stabilization involving a separation of charges. On the other hand, in II, there is stronger resonance stabilization of the molecule. Furthermore, there is neither intramolecular hydrogen bonding nor separation of charges but there is a delocalization of negative charge.



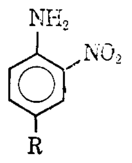
I



II



III



IV

It can be seen from Table I that a bathochromic shift in basic solution occurs for III → IV. One might expect stronger hydrogen bonding in III than in IV since there is a statistical factor of $^3/_2$ involved and the N-hydrogens in III are more acidic. Further, there is no resonance involving the H_3N^+ group in III, but there is resonance stabilization of IV involving separation of charges.

Therefore, since I and III are comparable as well as II and IV, then the wave number shifts for I → II and III → IV should be in the same direction but of different magnitudes. Experimental results show that the wave number shifts for III → IV are at least three times those for I → II. Furthermore, the spectral shifts for 4-substituted 2-chlorophenols[10] are approximately the same as for I → II. Thus, it is indicated that intramolecular hydrogen bonding is important in III → IV since it exists for all three series in acidic medium, but only for IV in basic medium.

An excellent correlation[3e,11a] has been obtained between the pK_A values and Hammett's σ for III as illustrated in eq. 1 and Figure 1. In eq. 1, −0.304 is

$$pK_A = -0.304 - \underset{(100.0)}{3.23}\sigma_p, \quad r = -0.992, \quad s = 0.21 \qquad (1)$$

the regression pK_A value for 2-nitroaniline, −3.23 is ρ, the Hammett reaction constant,[7a] σ_p is the Hammett substituent constant,[3f] r is the correlation coefficient, and s is the standard deviation from regression. In eq. 1–12, the number in parentheses below the coefficient of the independent variable is the percentage confidence level as determined by Student's t test.[11b] The negative value for ρ indicates that an electron-withdrawing substituent should increase the acidity of the respective anilinium ion.

One might expect, according to the additivity principle,[3g] that, if a fixed substituent Y is introduced *ortho* to the NH_2 group, as in V, the Hammett relationship would still be followed if the interaction between the NH_2 group and Y remains essentially constant as R is

---

[9] C. K. Hancock and A. D. H. Clague, *J. Am. Chem. Soc.*, **86**, 4942 (1964).

[10] H. N. Simpson, C. K. Hancock, and E. A. Meyers, *J. Org. Chem.*, **30**, 2678 (1965).

[11] G. W. Snedecor, "Statistical Methods," 5th Ed., The Iowa State College Press, Ames, Iowa, 1956: (a) Chapter 6; (b) pp. 46, 418, 441.

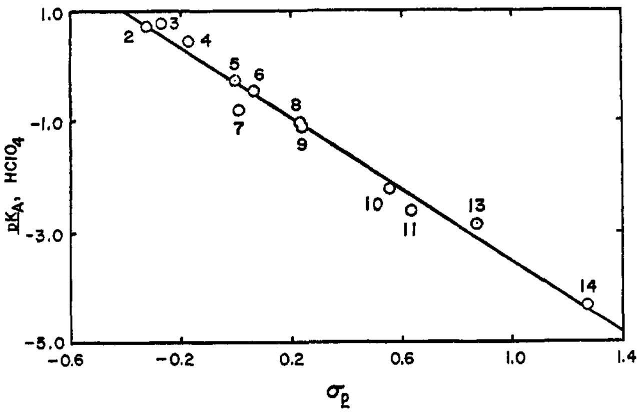


Figure 1.—The relationship between pK_A values in $HClO_4$ and σ_p for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table I.

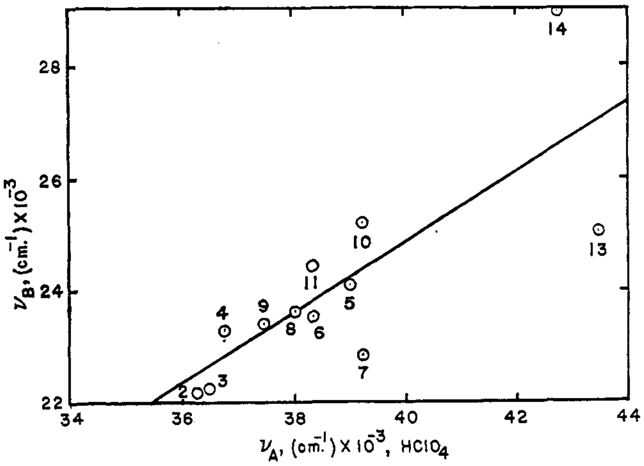
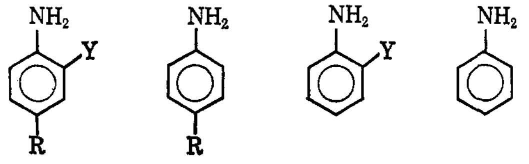


Figure 2.—The relationship between ν_B and ν_A in $HClO_4$ for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table I.

varied. That is, the reaction constants for V and VI should be the same under identical conditions with the effect of the constant *ortho* Y group being reflected in the pK_A of VII compared to the pK_A of VIII. The validity of this principle has been demonstrated for and for 4-substituted 2-chlorophenols.[10] However, I[6] slight variations in ρ were observed in the effect of a 2-methyl substituent on the ionization constants of 4- and 5-substituted benzoic acids[12] and the dissociation constants of 4-substituted 2,6-di-*t*-butylphenols.[13] In the present study of the pK_A values of III, the ρ value of -3.23 deviates from this principle, being significantly more negative than the ρ value of -2.77[8h] (-2.89[14]) for *meta*- and *para*-substituted anilines. This indicates that the electronic characteristics of the substituent are transmitted more effectively to the reaction site in III. Perhaps, some variation in ρ may occur when the solvation of the reaction site is implicated in the degree of ionization and the requirements for solvation of the reaction site may vary with the nature of R. Furthermore, it can be predicted that some variation in ρ should occur whenever there exists a significant interaction between the *ortho* substituent and the reaction site. Such interaction may be of two types, *viz.*, strong intramolecular hydrogen-bonding and solvation effects.



V VI VII VIII

That the value of ρ for the ionization of III should exhibit a deviation due to the first type of interaction can be demonstrated as follows. A substituent can affect the reaction site by a combination of polar, resonance, steric, and intramolecular hydrogen-bonding effects. In a series of 4-substituted 3-nitroanilines, the nitro group can affect the reaction site only by inductive effects. That this effect is constant throughout the series is verified by the fact that the ρ value for the regression of pK_A on σ for six 4-substituted 3-nitroanilines[15] is -2.83. This is in good agreement with the ρ value of -2.77 for VI. In a series of 5-substituted 4-nitroanilines, the nitro group can affect the reaction site by a combination of polar and resonance effects. If these effects are constant throughout the series, then the ρ value should be *ca.* -2.77 as for VI. Unfortunately, the pK_A values are not available for 5-substituted 4-nitroanilines. However, if the ρ value were about -2.77, this would indicate that the polar and resonance effects of the III are constant. Hence, the variable effect of the nitro group on the reaction site for IV would be due to either steric or intramolecular hydrogen-bonding effects or a combination of these.

The ρ value for the ionization of III shows a 17% deviation from that for the conjugate acid of VI. This is not an exceptionally large deviation when compared to the 57% deviation in water and 73% deviation in aqueous ethanol obtained for the ionization of 4-substituted 2,6-di-*t*-butylphenols[13] relative to 4-substituted phenols. However, the small deviation for III merits some explanation. Cohen and Jones[13] suggest that ionization and solvation at the hindered site are interrelated. In the case of III, the charge cannot be dispersed because there is no resonance involving the H_3N^+ group. However, in IV, if the lone pair of electrons is delocalized between the amino group and a strong *para* electron sink, the ease of ionization should be greatly increased. Hence, in this case, the size of the polar solvent sphere seems to be important in that it can aid the ionization. If sufficient data were available, it might be possible to add a substituent-dependent solvation term to the Hammett equation.

Thus, in the ionization equilibria between anilinium ions and aniline, the effect of the ionic solvating power of the solvent is particularly important and it seems reasonable that ρ for the stabilization of IV by solvent molecules could be different from that for VI.

In an attempt to compensate for this variation in ρ, the pK_A values were correlated with σ_p^+,[16] σ_m, and cross products of each of these independently with σ_p. No significance could be attached to any of the cross products. Furthermore, no contribution was made that was more significant than the original eq. 1.

---

[12] J. D. Roberts and J. A. Yancey, *J. Am. Chem. Soc.*, **73**, 1011 (1951).

[13] L. A. Cohen and W. M. Jones, *ibid.*, **85**, 3397 (1963).

[14] A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).

[15] A. R. Lawrence and L. N. Ferguson, *J. Org. Chem.*, **25**, 1220 (1960).

[16] H. C. Brown and Y. O. Okamoto, *J. Am. Chem. Soc.*, **80**, 4980 (1958).

For III, there is no correlation ($r = 0.196$) between pK_A and $\Delta\nu$ (the basic wave number shift, *i.e.*, $\nu_B - \nu_A$). The reasons for this poor relationship are probably the same as those discussed previously for 4-substituted 2-nitrophenols.[6]

The fair correlation between ν_B and ν_A, the wave numbers of IV and III, is shown in eq. 2 and Figure 2.

$$\nu_B = -306 + 0.627\nu_A,\ r = 0.790,\ s = 1162 \quad (2)$$
$$(99.8)$$

Apparently, the substituents play similar roles in fulfilling the electron-demand requirements of both the ν_B and ν_A series. Hence, each series may be treated independently with respect to substituent effects as shown in eq. 3 and 4 and Figures 3 and 4. In the case

$$\nu_B = 23{,}200 + 3390\sigma_p,\ r = 0.911,\ s = 780 \quad (3)$$
$$(100.0)$$

$$\nu_A = 37{,}700 + 3990\sigma_p,\ r = 0.853,\ s = 1240 \quad (4)$$
$$(100.0)$$

of I, an excellent correlation was obtained between $\sigma_p{}^+$ and ν_A or ν_B. The use of $\sigma_p{}^+$ in the case of 4-substituted 2-chlorophenols[10] gave no improvement. Likewise, no significant improvement was obtained in the case of IV.

No significant relationship was found between $\Delta\nu$ and σ_p or $\sigma_p{}^+$.

Substantiating the conclusions of previous studies in this area,[6,9,10] correlation of primary absorption bands of IV with structure by eq. 3 and 4 is only fair.

Investigation of the Polarographic Reduction and Oxidation of 4-Substituted 2-Nitroanilines.—Previous studies[17–19] indicate that aromatic electron-withdrawing substituents favor reduction at the dropping mercury electrode (d.m.e.). The reduction of aromatic nitro compounds at the d.m.e. has been postulated[20] to go to completion with the formation of the amine. This would involve six electrons and should give a single wave. In view of the preceding, it seemed desirable to investigate the behavior of IV at the d.m.e. since the nitro group in IV is strongly electron-withdrawing and its reducibility at the d.m.e. should be affected by the nature of the 4-substituent.

The polarographic reduction half-wave potentials for 13 compounds of type IV were determined in 75% aqueous ethanol with KNO_3 as supporting electrolyte and are listed in Table II. The correlation coefficient between $E_{1/2}$ and σ_m of 0.606 shows that only 37% of the variation in $E_{1/2}$ is accounted for by the regression equation; consequently, little can be said as to the polar effect of a particular substituent on the half-wave potential. This poor correlation may be partially due to changes in the reaction mechanism, the number of electrons transferred, or the value of the transfer coefficient. Presently, studies are being made[21] of the dependence of $E_{1/2}$ on pH in order to ascertain if the first two changes are important.

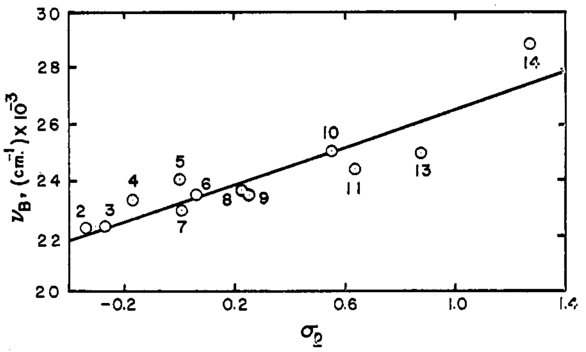


Figure 3.—The relationship between ν_B and σ_p for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table I.

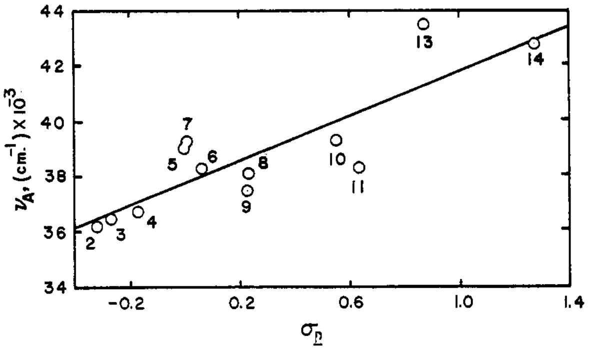


Figure 4.—The relationship between ν_A in $HClO_4$ and σ_p for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table I.

The polarographic oxidation of IV was investigated at the rotating platinum electrode in acetonitrile and in methanol–sodium acetate–hydrochloric acid buffer solutions.[22] All attempts to obtain oxidation waves failed. Recently,[23] it has been shown that *meta-* and *para-*substituted anilines have oxidation half-wave potentials in the region +0.80 to +0.72 v. The nitro group in IV probably diminishes the ease of oxidation of the amino group. This is reasonable since a solution of aniline will decolorize upon standing while a solution of *o*-nitroaniline is stable over a long period of time.

TABLE II

POLAROGRAPHIC REDUCTION POTENTIALS OF 4-SUBSTITUTED 2-NITROANILINES

4-Substituent	σ_m[a]	$E_{1/2}$, v. (*vs.* s.c.e.)[b]
NH_2	−0.161	−0.81
CH_3	−0.069	−0.84
H	0.000	−0.93
OCH_3	0.115	−0.79
C_6H_5	0.218	−0.84
$COCH_3$	0.306	−0.84
$COOCH_3$	0.315	−0.82
F	0.337	−0.76
Cl	0.373	−0.74
CHO	0.382	−0.81
Br	0.391	−0.74
CF_3	0.415	−0.84
NO_2	0.710	−0.71

[a] All σ_m values are from ref. 3f. [b] Value quoted is the average of three determinations. In each case, the average deviation from the mean value was less than 0.02 v.

---

(17) M. Shikata, *Trans. Faraday Soc.*, **21**, 42 (1925).

(18) M. Shikata and I. Tachi, *J. Chem. Soc. Japan*, **53**, 834 (1932).

(19) R. W. Brockman and D. E. Pearson, *J. Am. Chem. Soc.*, **74**, 4128 (1952).

(20) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, p. 748.

(21) P. Y. Rodriguez, M.S. research in progress, Texas A & M University.

(22) G. E. Panketh, *J. Appl. Chem.*, **7**, 512 (1957).

(23) W. R. Carper, R. M. Hedges, and H. N. Simpson, *J. Phys. Chem.*, **69**, 1707 (1965).

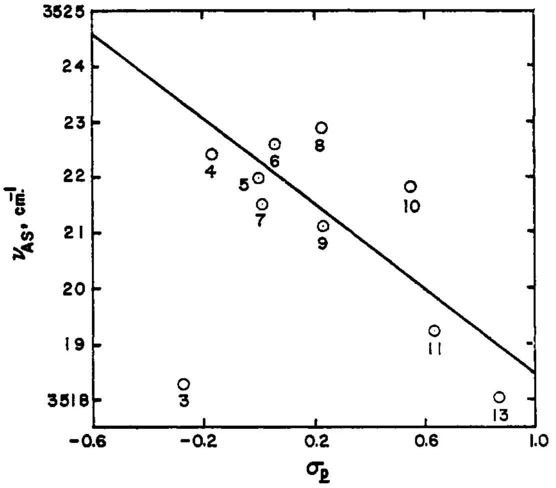


Figure 5.—The relationship between ν_{AS} and σ_p for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table III.

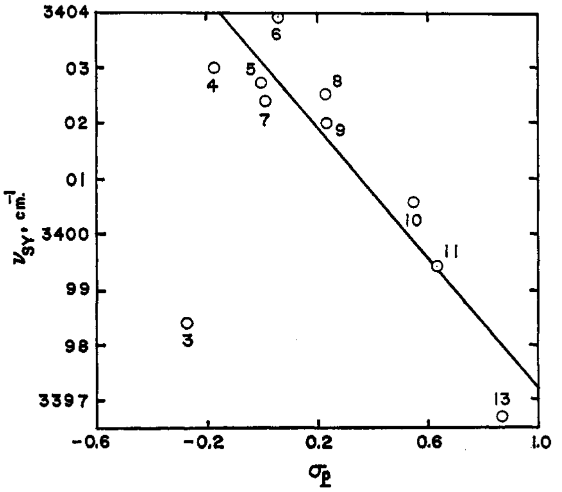


Figure 6.—The relationship between ν_{SY} and σ_p for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table IV.

Since IV might degrade before the half-wave could be obtained, the synthesis[24] of o-nitro-β-phenylhydroxylamine was attempted in order to study its polarographic oxidation. However, this compound was not isolated in pure form. The contaminants were probably o-nitroazobenzene and o-nitroazoxybenzene.

Furthermore, a 0.1 N solution of o-nitroaniline was titrated potentiometrically with 0.1 N $KMnO_4$. No large change in potential, other than that produced by the initial addition of $KMnO_4$ to o-nitroaniline, could be detected. Evidently, although $KMnO_4$ is a strong oxidizing agent, it is not strong enough to oxidize o-nitroaniline.

Since compounds of structure IV have both oxidizable and reducible groups, they should theoretically give both oxidation and reduction half-wave potentials. Even though no Hammett relationship was found for the polarographic reduction of IV and attempts to measure polarographic oxidation half-wave potentials of IV failed, it is still believed that a suitable combination of electronic spectral data and polarographic reduction and oxidation half-wave potentials for an appropriate series of compounds might lead to theoretically significant conclusions. Electronic spectral data are already available for 4-substituted[6] and 5-substituted[9] 2-nitrophenols and polarographic reduction and oxidation studies of these two series are in progress.[21]

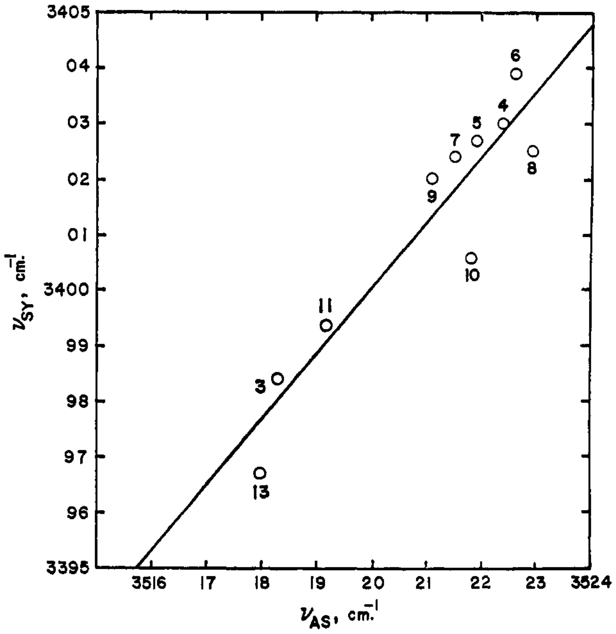


Figure 7.—The relationship between ν_{SY} and ν_{AS} for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Tables III and IV.

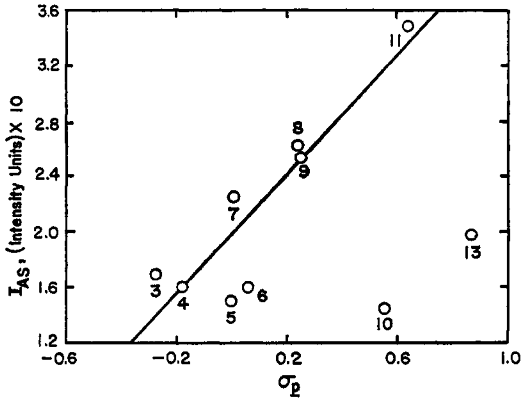


Figure 8.—The relationship between I_{AS} and σ_p for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table III.

Infrared Spectral Studies of 4-Substituted 2-Nitroanilines.—The O–H stretching frequencies for substituted catechols and phenols[25] and the first and second overtones of the N–H stretching vibrations of some primary aromatic amines[26] have been correlated with σ. Also,[27] the integrated band areas of the fundamental stretching mode of the N–H group of anilines and anilides have been correlated with structural characteristics and polar properties of the N–H group, and marked differences between compounds of different classes have been observed. In view of the preceding, it was decided to study the relationship between σ and the fundamental N–H stretching frequencies or

---

[24] R. Kuhn, H. Vettwe, and P. Desnuelle, *Ber.*, **B70**, 1314 (1937).

[25] L. L. Ingraham, J. Corse, G. F. Bailey, and F. Stitt, *J. Am. Chem. Soc.*, **74**, 2297 (1952).

[26] K. B. Whetsel, W. E. Roberson, and M. W. Krell, *Anal. Chem.*, **30**, 1598 (1958).

[27] R. A. Russell and H. W. Thompson, *J. Chem. Soc.*, 483 (1955).

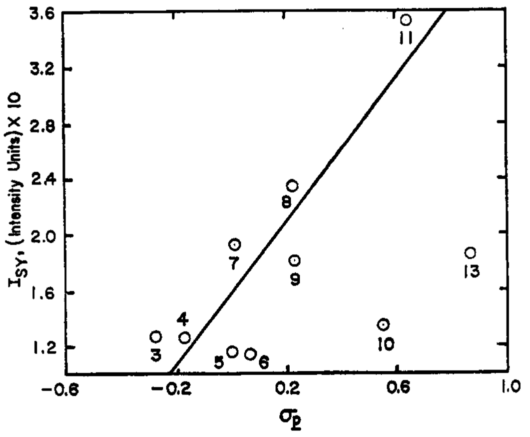


Figure 9.—The relationship between I_{SY} and σ_p for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table IV.

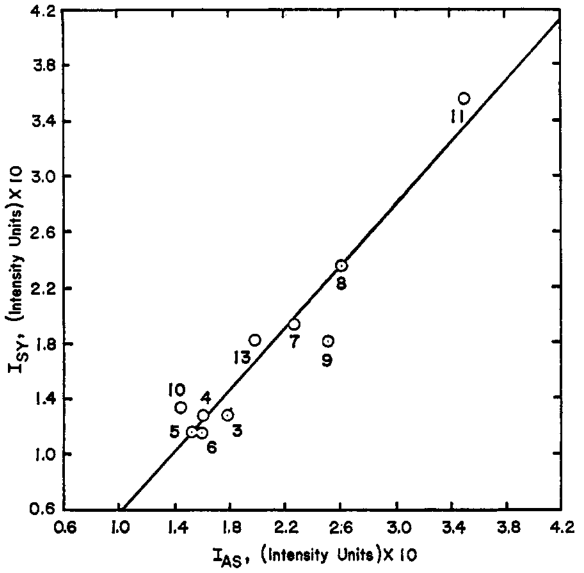


Figure 10.—The relationship between I_{SY} and I_{AS} for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Tables III and IV.

band intensities of IV, since they occur free from overlapping bands.

In dilute solution, primary amines give absorption bands[28] near 3500 (asymmetric stretching mode) and 3400 cm.$^{-1}$ (symmetric stretching mode). Both of these vibrations are subject to small changes with alteration of the polarity of the solvent or intramolecular hydrogen bonding.

The data in Tables III and IV for the asymmetric and symmetric frequencies were correlated[3e,11a] with σ_p. For each frequency, the deviation from regression for the *p*-methoxy compound **3** is nearly twice the standard deviation. Omitting the data for **3**, regression analyses gives the fairly good relationships shown in eq. 5 and 6 and Figures 5 and 6.

$$\nu_{AS} = 3523 - 3.84\sigma_p,\ r = -0.809,\ s = 1.03 \quad (99.2) \qquad (5)$$

$$\nu_{SY} = 3403 - 5.95\sigma_p,\ r = -0.923,\ s = 0.92 \quad (100.0) \qquad (6)$$

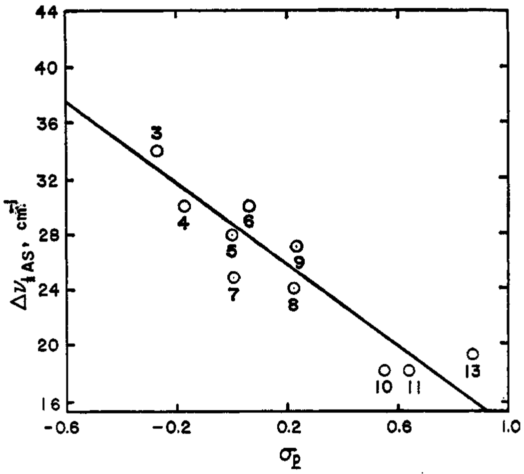


Figure 11.—The relationship between $\Delta\nu_{1/2\mathrm{AS}}$ and σ_p for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table III.

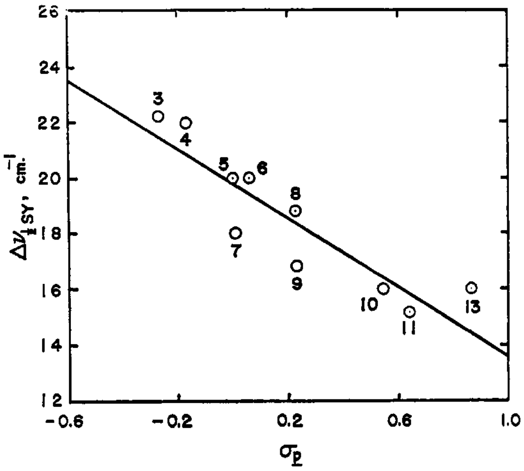


Figure 12.—The relationship between $\Delta\nu_{1/2\mathrm{YS}}$ and σ_p for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table IV.

Table III

Infrared Spectral Data for 4-Substituted 2-Nitroanilines. Asymmetric Band

Compd.	4-Substituent	σ_p[a]	Concn., $M \times 10^2$	Log $\left(\frac{T_0}{T}\right)_{\nu_{max}}$	$\Delta\nu_{1/2}$, cm.$^{-1}$	ν, cm.$^{-1}$	I[b]
3	OCH_3	−0.268	5.02	1.73	34.0	3518.3	0.178
4	CH_3	−0.170	5.04	1.77	30.0	3522.4	0.160
5	H	0.000	5.01	1.79	28.0	3522.0	0.152
6	F	0.062	5.08	1.79	30.0	3522.6	0.160
7	C_6H_5	0.009	2.56	1.53	24.8	3521.5	0.225
8	Cl	0.227	2.05	1.48	24.0	3522.9	0.262
9	Br	0.232	2.54	1.55	27.2	3521.1	0.252
10	CF_3	0.551	3.47	1.81	18.0	3521.8	0.143
11	CO_2CH_3	0.636	1.00	1.28	18.0	3519.2	0.349
13	$COCH_3$	0.874	2.55	1.72	19.2	3518.0	0.196

[a] All σ_p values are from ref. 3f. [b] By convention, 1×10^4 mole^{-1} l. cm.$^{-2}$ is designated as one intensity unit.

The correlation between the asymmetric and symmetric stretching frequencies is shown in eq. 7 and

$$\nu_{SY} = -804 + 1.19\nu_{AS},\ r = 0.935,\ s = 0.870 \quad (100.0) \qquad (7)$$

Figure 7. This good relationship is somewhat expected since the asymmetric and symmetric stretching frequencies depend to some extent upon a common factor, *viz.*, the polar character of the substituent.

---

[28] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Chapter 14.

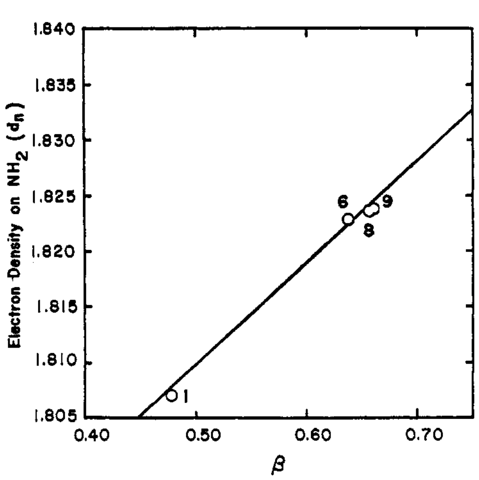


Figure 13.—The relationship between d_n and β for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table V.

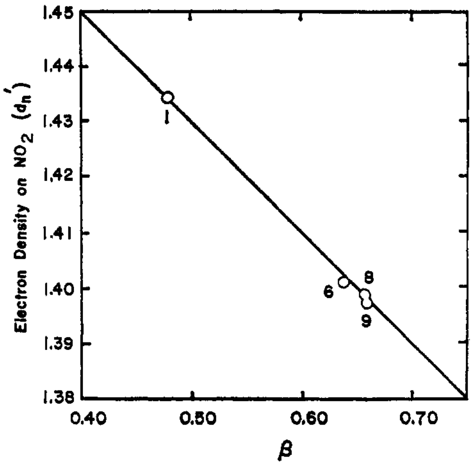


Figure 14.—The relationship between d_n' and β for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table V.

TABLE IV

INFRARED SPECTRAL DATA FOR 4-SUBSTITUTED 2-NITROANILINES. SYMMETRIC BAND

Compd.	4-Substituent	σ_p[a]	Concn., $M \times 10^2$	Log $\left(\frac{T_0}{T}\right)_{\nu_{max}}$	$\Delta\nu_{1/2}$, cm.$^{-1}$	ν_j cm.$^{-1}$	I[b]
3	OCH_3	−0.268	5.02	1.91	22.2	3398.4	0.128
4	CH_3	−0.170	5.04	1.92	22.0	3403.0	0.127
5	H	0.000	5.01	1.94	20.0	3402.7	0.117
6	F	0.062	5.08	1.94	20.0	3403.9	0.116
7	C_6H_5	0.009	2.56	1.82	18.0	3402.4	0.194
8	Cl	0.227	2.05	1.70	18.8	3402.5	0.236
9	Br	0.232	2.54	1.80	16.8	3402.0	0.181
10	CF_3	0.551	3.47	1.96	16.0	3400.6	0.137
11	CO_2CH_3	0.636	1.00	1.54	15.2	3399.4	0.356
13	$COCH_3$	0.874	2.55	1.93	16.0	3396.7	0.184

[a] Ref. *a*, Table III. [b] Ref. *b*, Table III.

Only a fair relationship was obtained between pK_A and the asymmetric or symmetric frequencies. This poor fit is due to the fact that the N-H frequencies are properties of the bases alone, whereas pK_A values are determined by the substituent effects on both the acid and base components of the system, and the relative importance of resonance and polar effects in these will not necessarily remain constant as the substituent changes its type.

In an attempt to supplement the frequency measurements, the intensities of the bands were also obtained. Quantum mechanically, the intensity of a transition between two energy states of a molecule is proportional to an integral of form IX and the frequency of the transition is proportional to an integral of form X, where ψ' and ψ'' are the wave functions for the ground

$$\underset{\text{IX}}{\int \psi'(\text{er})\psi''\text{d}\tau} \qquad \underset{\text{X}}{\int \psi'\text{H}\psi'\text{d}\tau}$$

and excited states, respectively, and er and H are the quantum operators. From variation theory considerations, it can be seen that the frequency has essentially a second-order dependence on ψ', whereas, the intensity has a first-order dependence on ψ'. Thus, one may expect to see a greater sensitivity of the intensities than of the frequencies in correlation with σ.

Consequently, the equations for the regression of the intensities of the asymmetric or symmetric frequencies on σ were obtained. However, in both cases the 4-CF_3 and 4-$COCH_3$ compounds show deviations which are nearly twice the standard deviation. These were omitted in the next analyses and the fairly good correlations shown in eq. 8 and 9 and in Figures 8 and 9 were obtained.

$$I_{AS} = 0.197 + \underset{(99.6)}{0.217\sigma_p}, \; r = 0.884, \; s = 0.035 \qquad (8)$$

$$I_{SY} = 0.158 + \underset{(99.6)}{0.260\sigma_p}, \; r = 0.880, \; s = 0.042 \qquad (9)$$

The good relationship between the intensities of the asymmetric band and of the symmetric band shown in eq. 10 and Figure 10 is expected for the reason given previously for the correlation of eq. 7.

$$I_{SY} = -0.049 + \underset{(100.0)}{1.092I_{AS}}, \; r = 0.956, \; s = 0.023 \qquad (10)$$

Finally, the fairly good correlation between the apparent half-band widths of the asymmetric or of the symmetric stretching bands and σ are shown in eq. 11 and 12 and Figures 11 and 12.

$$\Delta\nu^1/_{2AS} = 28.3 - \underset{(100.0)}{13.7\sigma_p}, \; r = -0.912, \; s = 2.41 \qquad (11)$$

$$\Delta\nu^1/_{2SY} = 19.8 - \underset{(100.0)}{6.14\sigma_p}, \; r = -0.898, \; s = 1.18 \qquad (12)$$

The Hückel Molecular Orbital (HMO) Treatment of Some 4-Substituted 2-Nitroanilines.—In the HMO method, Coulomb (α) and resonance (β) integrals are regarded as parameters and overlap integrals are assumed to be zero. Heteroatoms may be treated by appropriate changes in the empirical α and β parameters associated with each atom and bond. HMO calculations were performed by Wiberg's program[29] as modified by R. M. H. to provide greater facility in loading heteroatom matrix elements. Differential overlap was neglected. Heteroatom matrix elements were treated as

$$\alpha_x = \alpha_c + h_x\beta_{cc}$$

$$\beta_{cx} = k_x\beta_{cc}$$

where α_c and β_{cc} are the "standard" Coulomb and resonance integrals of an atom and the bond, respectively, in benzene and α_x and β_{cx} are the Coulomb and

---

(29) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p. 577.

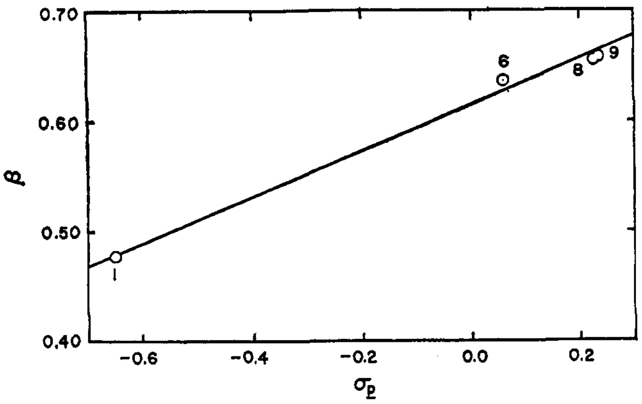


Figure 15.—The relationship between β and σ_p for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table V.

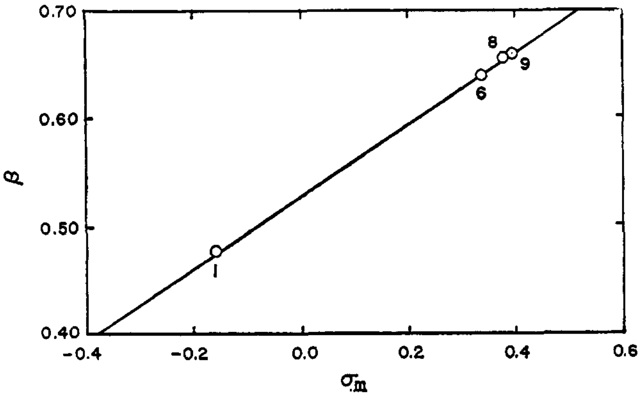


Figure 16.—The relationship between β and σ_m for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table V.

resonance integrals of an atom adjacent to a heteroatom. The heteroatom parameters (h_x and k_x) of Streitwieser[30] were used.

The results of the HMO calculations are given in Table V and show excellent correlations between the β coefficients for the highest filled energy level and the π-electron densities on the amino nitrogen atom (d_n) or the π-electron densities on the nitro nitrogen atom (d_n') as can be seen in Figures 13 and 14.

Table V

HMO Calculations for 4-Substituted 2-Nitroanilines

Compd.	4-Substituent	σ_p[a]	σ_m[a]	No. of π centers	β coefficients	Amino nitrogen π-electron density (d_n)	Nitro nitrogen π-electron density (d_n')
5	H	0.000	0.000	12	0.6833	1.8244	1.3957
6	F	0.062	0.337	14	0.6371	1.8228	1.4010
8	Cl	0.227	0.373	14	0.6567	1.8235	1.3984
9	Br	0.232	0.391	14	0.6594	1.8236	1.3979
1	NH_2	−0.660	−0.161	14	0.4786	1.8070	1.4343

[a] All σ_p and σ_m values are from ref. 3.

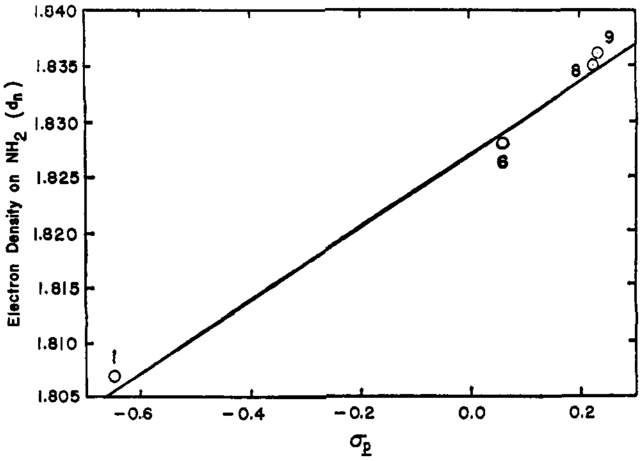


Figure 17.—The relationship between d_n and σ_p for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table V.

Further, there are linear relationships between the appropriate β coefficients and σ as shown in Figures 15 and 16 and between the π-electron densities and σ as shown in Figures 17 and 18. Thus, it appears that σ may be taken as a measure of the over-all electronic description of this molecular series rather than being a description of localized electronic interactions.

Experimental Section

The 4-substituted 2-nitroanilines which were commercially unavailable were prepared by methods previously reported in the literature, as indicated by footnotes to Table VI.

Table VI

Melting Points of 4-Substituted 2-Nitroanilines

4-Substituent	M.p., °C.[a]	Lit. m.p., °C.
OCH_3	122–123	122–123[b,c]
OC_4H_9	65–66	66[d]
CH_3	114–115	114[e,c]
C_6H_5	164–165	167–169[f]
CF_3	106–107	106–107[g]
CO_2CH_3	196–197.5	196–198[h,i]
$COCH_3$	149–151	148–149[j]
CHO	186–187	190–191[k]
Cl	114–115	116[l,c]
F	92.5–93	92.5[m]
Br	109	110–111[n]
H	71–72.5	71.5[o,c]
NH_2	135.5–137	136–138[p,c]
NO_2	179–180	180[q,c]

[a] Corrected. [b] A. Izmailškii and A. M. Simonov, *J. Gen. Chem. USSR*, **10**, 1580 (1940). [c] Obtained commercially. [d] A. W. Baldwin and R. Robinson, *J. Chem. Soc.*, 1264 (1934). [e] L. Gindraux, *Helv. Chim. Acta*, **12**, 921 (1929. [f] E. Berliner, B. Neuman, and T. M. Riaboff, *J. Am. Chem. Soc.*, **77**, 478 (1955). [g] R. Long and A. L. Morrison, *J. Chem. Soc.*, 3852 (1954). [h] P. R. Thomas and G. J. Tyler, *ibid.*, 2197 (1957). [i] Prepared by esterification of 4-carboxy-2-nitroaniline. [j] C. S. Gibson and B. Levin, *J. Chem. Soc.*, 2388 (1931). [k] H. H. Hodgson and H. G. Beard, *ibid.*, 23 (1927). [l] E. Crepaz, *Atti ist. veneto sci.*, **94**, 555 (1934). [m] F. K. Beilstein, "Handbuch der Organischen Chemie," 4th Ed., J. Springer, Berlin, 1920, 12 1, p. 355. [n] Footnote *m*, 12, p. 737; I, p. 358; II, p. 401. [o] I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1953, p. 628. [p] W. Ruske, *Ann.*, **610**, 143 (1957). [q] Footnote *o*, p. 362.

Ultraviolet Spectral Studies and Measurement of pK_A Values of 4-Substituted 2-Nitroanilines.—The absorption spectra and pK_A values of 0.0001 *M* solutions of IV were measured as described previously[6] and are shown in Table I. The Beckman DK-1 spectrophotometer was calibrated as described previously.[10] However, instead of buffer solutions, perchloric acid solutions of varying concentrations were used. Owing to low solubility in water, compounds **2**, **7**, **11**, **13**, and **14** in Table I were dissolved in 25 ml. of absolute ethanol and then diluted to 1 l. with de-

---

(30) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 135.

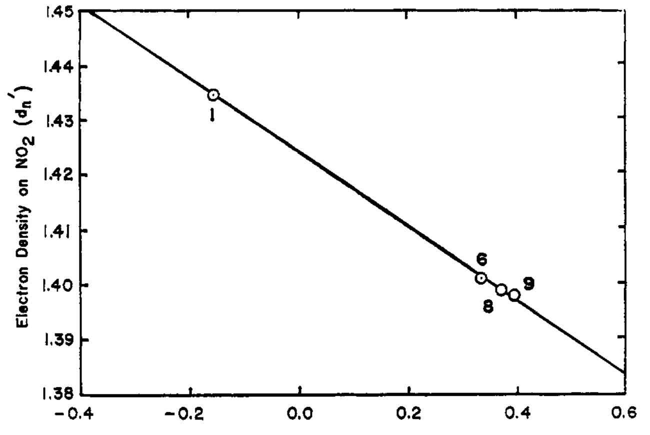


Figure 18.—The relationship between d_n' and σ_m for 4-substituted 2-nitroanilines. Numbers refer to compounds listed in Table V.

ionized water. The spectra of these five solutions were measured against reference solutions of aqueous ethanol of the same concentration.

The pK_A values were calculated from the equation[7b] where A

$$pK_A = H_0 - \log \frac{A - A_1}{A_2 - A}$$

is the absorbance of the solution containing varying concentrations of aqueous $HClO_4$, A_1 is the absorbance of the solution in 70% $HClO_4$, A_2 is the absorbance of the base solution, and H_0[31] is the acidity function.

Polarographic Reductions of Some 4-Substituted 2-Nitroanilines.—A 0.005 *M* solution (10 ml.) of IV in 75% aqueous ethanol plus 10 ml. of 1 *M* KNO_3 solution were diluted to 100 ml. with deionized water. A portion of this solution was transferred to the cathode compartment of a three-compartment polarography cell, the center compartment containing 1 *M* KNO_3 solution, and the anode compartment containing a saturated calomel electrode. The compartments were separated by plugs of agar. The solution of IV was purged with nitrogen and the polarogram was obtained with a Sargent Model XXI polarograph. The reduction half-wave potentials shown in Table II were obtained by the point method.[32]

Infrared Spectral Studies and Measurement of Intensities of 4-Substituted 2-Nitroanilines.—The N-H stretching bands of IV were measured with a Beckman IR-9 infrared spectrometer. A variable path length cell was initially used to balance out solvent absorption. Matched absorption cells of the sandwich type containing sodium chloride prisms were used.

A 0.05 *M* solution of IV was prepared in spectroquality chloroform. The absorption spectra were measured over a wavenumber range of 50 cm.$^{-1}$ on either side of the band center. The N-H stretching band was expanded five times.

The absorption intensity, *I*, was obtained from the relation[33]

$$I = \frac{K}{cl}\left[\log\left(\frac{T_0}{T}\right)_{\nu_{\max}}\right]\Delta\nu_{1/2}$$

The area under the curve was obtained by the triangular method, *i.e.*, the peak height times the band width at one-half the peak height. The results are shown in Tables III and IV.

Acknowledgment.—This study was supported in part by a research grant from the Robert A. Welch Foundation. Helpful discussions of the results with Dr. Edward A. Meyers are gratefully acknowledged. The statistical calculations were performed by the Data Processing Center, Texas Engineering Experiment Station, College Station, Texas, on an IBM-709 computer.

---

[31] M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

[32] H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, "Instrumental Methods of Analysis," D. Van Nostrand Co., Inc., Princeton, N. J., 1958, p. 544.

[33] D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952). From Table III, the value of *K* equals 1.57.

Mass Spectra of Porphyrins and Chlorins

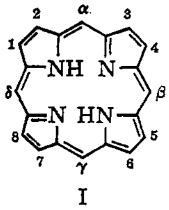
DONALD R. HOFFMAN

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

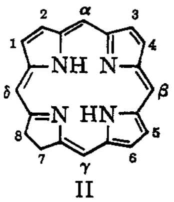
Received May 16, 1965

The mass spectra of several porphyrins and chlorins of synthetic and biological interest have been obtained and interpreted. These compounds fragment only peripherally as one would expect of a large aromatic system. Substituents in the 7- and 8-positions in chlorins are more labile than pyrrole ring substituents. γ-Substituents are even more labile and are lost with the transfer of one and two hydrogens to the tetrapyrrole system, if possible. A steric effect is observed in the loss of γ-substituents. The spectra of compounds containing additional five- and six-membered carbocyclic rings, including methyl phaeophorbide, were obtained and interpreted. The directions of ring closure predicted for two isomeric chlorins in Woodward's chlorophyll synthesis were confirmed. The mass spectra of several compounds containing six-membered lactone rings are discussed. Mechanisms are proposed for several of the types of fragmentations observed.

Porphyrins (I) and chlorins (II) are very difficult compounds to handle in the laboratory. Many of them are very complex and quite reactive. The verification of their structures has always been a major problem, since many classical methods cannot always give unambiguous results. Infrared and ultraviolet absorption spectra provided some information, but it was not always definitive. Recently n.m.r. spectroscopy has been shown to be a useful tool for investigating the structures of these compounds,[1] but many interesting tetrapyrrole compounds are not soluble enough to give good spectra. Additional methods are very much needed in this field because of the immense biological importance of these compounds in both plants and animals. The chlorins are in many ways quite similar to the porphyrins, but in others they are quite different.[2] See Table I for compounds studied.



I



II

---

[1] R. B. Woodward and V. Skaric, *J. Am. Chem. Soc.*, **83**, 4676 (1961).

[2] R. B. Woodward, *Ind. chim. belge*, **27**, 1293 (1962).