was separated from the aqueous layer by centrifugation (brilliant green product) or extraction with ether (crystal violet product). When ether was used, the extractions were combined and dried over sodium carbonate. Attempts to crystallize the products from aqueous ethanol either failed or were impractical because the products weighed so little. The products were prone to reoxidation during work-up procedures. Specific details for individual compounds are given below.

Brilliant green (1 mmol, 421 mg based on the chloride) was refluxed for 21 days and nights with 100 mmol (10.4 g) of sodium bisulfite ($NaHSO_3$). The crude product was a black oil. The purified product was a viscous and colorless oil which tended to turn green and weighed 140 mg (36% yield).

The nmr spectrum (d_6-acetone) exhibited a singlet at 7.25 (aromatic C–H), a quartet at 6.83 (*para*-substituted aromatic C–H), a singlet at 5.34 (triphenylmethane C–H), a quartet at 3.36 (aliphatic CH_2), and a triplet at 1.12 ppm ($C-CH_3$). The integrated intensity ratio of these bands was 5:8:1:8:12.

Crystal violet (1 mmol, 408 mg based on the chloride) was refluxed with 300 mmol (31.22 g) of sodium bisulfite for 4 days and nights. The crude product (white needles, solutions of which turned blue) weighed 31 mg (8.3%).

The nmr spectrum (d_6-acetone) showed a quartet at 6.81 (*para*-substituted aromatic C–H), a singlet at 5.22 (triphenylmethane C–H), and a singlet at 2.86 ppm ($N-CH_3$). The integrated intensity ratio for these bands was 12:1:18.

The effect of bisulfite concentration on the yield of leuco base was investigated in another experiment. Crystal violet (1 mmol, 408 mg) was refluxed 14 days and nights with 100 mmol (10.4 g) of sodium bisulfite. The fatigued solution was worked up as described to yield 7 mg (1.8%) of white needles similar with those above. The yield, as well as the bisulfite concentration, was thus lower than in the previous experiment.

The effect of hydrogen gas on the yield of leuco base was also investigated. Crystal violet (1 mmol, 408 mg) was dissolved with 100 mmol (10.4 g) of sodium bisulfite in 300 ml of water and placed in a Parr hydrogenation vessel. The bottle was charged with 10 lb of hydrogen gas using the normal procedure and shaken for 8 hr at room temperature. No leuco base product could be isolated by the usual isolation procedure.

Another solution identical with the first was prepared and heated at about 50° under 10–15 lb of hydrogen gas pressure in the Parr hydrogenator for 5 days and nights. When cooled and extracted with ether the mixture yielded only 5 mg of impure residue which turned blue indicating that leuco base was present.

Two other solutions were prepared similarly and refluxed in open vessels for about 3 days and nights with hydrogen gas passing through the solutions. The yields of crude product isolated in these experiments was 10 and 12 mg, not significantly higher than the 7-mg yield obtained without the added hydrogen.

Registry No.—I, 16097-04-4; II, 16097-05-5; III, 16097-06-6; IV, 16097-07-7; V, 16097-08-8.

The Correlation of the Electronic Spectra and Acidity of 5-Substituted 2-Nitroanilines with Structure[1]

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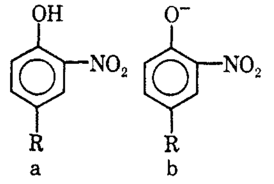
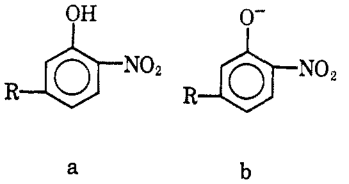
Received March 13, 1967

The electronic spectra and pK_a's of a series of 5-substituted 2-nitroanilines (IV) have been measured. An excellent correlation exists between the resulting pK_a's and Hammett's σ_m. Structure–spectra correlations for this series are compared with corresponding correlations for 4-substituted 2-nitroanilines (III), 4-substituted 2-nitrophenols (I), and 5-substituted 2-nitrophenols (II). Good correlations exist between the absorption frequencies of I and those of the isoelectronic III, and between the absorption frequencies of II and those of the isoelectronic IV.

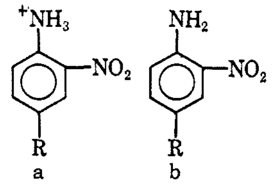
Excellent acidity–structure correlations have been reported previously for thirteen 4-substituted 2-nitrophenols[3] (I), eleven 5-substituted 2-nitrophenols[4] (II), and twelve 4-substituted 2-nitroanilines[5] (III). On the other hand, there is very little uniformity in electronic spectra–structure correlations for these three series of compounds.



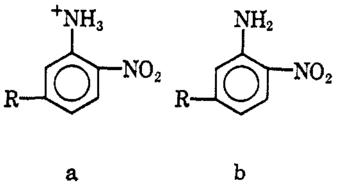
I



II



III



IV

The structural relationship between the 5-substituted 2-nitroanilines (IV) and III is the same as that between II and I. In view of this fact and of the different spectra–structure correlations found for II[4] compared to those for I,[3] it appeared to be of interest to measure and correlate the electronic spectra and acidities of IV and to compare the results with those found[5] for III.

Results and Discussion

The electronic spectra and pK_a's of a series of six 5-substituted 2-nitroanilines (IV) have been measured and the results are shown in Table I.

For IVa in aqueous solution, there is an excellent correlation[6a] between the pK_a's and Hammett's σ_m constants[7] as shown by eq 1 and Figure 1. For eq 1,

$$pK_a = -0.296 - 3.10\,\sigma_m \quad \overset{r}{-0.999} \quad \overset{s}{0.051} \quad 100.0\% \qquad (1)$$

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[1] Abstracted in part from the results of undergraduate research of R. A. B.

[2] To whom inquiries should be sent.

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

[4] C. K. Hancock and A. D. H. Clague, *ibid.*, **86**, 4942 (1964).

[5] J. O. Schreck, C. K. Hancock, and R. M. Hedges, *J. Org. Chem.*, **30**, 3504 (1965).

[6] G. W. Snedecor, "Statistical Methods," 5th ed, The Iowa State College Press, Ames, Iowa, 1956: (a) Chapter 6; (b) pp 46, 418, and 441; (c) Chapter 14.

[7] H. H. Jaffé, *Chem. Rev.*, **53**, 222 (1953).

TABLE I

ACIDITY AND SPECTRAL DATA FOR SIX 5-SUBSTITUTED 2-NITROANILINES

No.	Registry no.	5-Substituent	pK_a[a]	λ_b,[b] mμ	ν_b[c] × 10^{-4}, cm^{-1}	ϵ_b[d] × 10^{-3}	λ_a,[e] mμ	ν_a[f] × 10^{-4}, cm^{-1}	ϵ_a[g] × 10^{-3}	$\Delta\nu$[h] × 10^{-4}	σ_m[i]
1	578-46-1	CH_3	−0.09 (−0.21)	412	2.43	4.84	286	3.50	7.64	−1.07	−0.069
2	88-74-4	H	−0.23 (−0.34)	413	2.42	4.54	266	3.76	6.98	−1.34	0.000
3	16133-49-6	OCH_3	−0.72 (−0.83)	400	2.50	6.04	323	3.10	9.07	−0.60	0.115
4	1635-61-6	Cl	−1.48 (−1.57)	407	2.46	5.22	282	3.55	8.88	−1.09	0.373
5	5228-61-5	Br	−1.48 (−1.57)	407	2.46	5.29	284	3.52	10.07	−1.06	0.391
6	619-18-1	NO_2	−2.49 (−2.52)	440	2.27	4.30	263	3.80	10.73	−1.53	0.710

[a] For each compound, the first pK_a value was measured in aqueous solution, and the second pK_a value (in parentheses) was measured in solution in 10 vol % aqueous ethanol. [b] λ_b (mμ) = λ_{max}^{NaOH}. [c] ν_b (cm^{-1}) = $(1/\lambda_b) \times 10^7$. [d] ϵ_b = extinction coefficient in basic 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 acidic solution. [h] $\Delta\nu = \nu_b - \nu_a$. [i] Reference 7a.

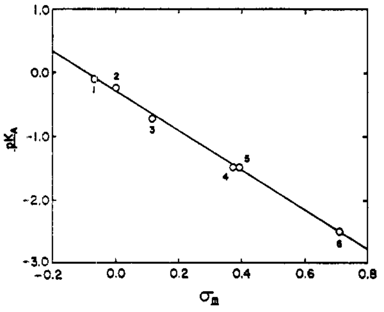

Figure 1.—The relationship between pK_a values in $HClO_4$ and σ_m for six 5-substituted 2-nitroanilines. Numbers refer to compounds listed in Table I.

r is the linear correlation coefficient, s is the standard deviation from regression, and 100.0% is the percentage confidence level based on Student's t (test).[6b] The ρ_m value of −3.10 found for IVa is more positive than the ρ_p value of −3.23 found[5] for IIIa, while the ρ_m value of −3.01[4] for IIa is more negative than the ρ_p value of −2.16[3] for Ia.

As shown previously[4] by a multiple regression analysis[6c] of the data for IIa, the 5-substituent exerts a small, but significant, $\sigma_p{}^+$ [8] effect on the pK_a of IIa which indicates that there is direct resonance interaction between the 5-substituent and the 2-nitro group. Multiple regression analysis of the present data for IVa gives eq 2 where R is the multiple correlation coefficient.[6c]

$$\begin{array}{lccc} \mathrm{p}K_a = -0.251 - \underset{(100.0\%)}{3.27\sigma_m} + \underset{(93.5\%)}{0.123\sigma_p{}^+} & \overset{R}{1.000} & \overset{s}{0.031} & (2) \end{array}$$

Eq 2 indicates that $\sigma_p{}^+$ is not statistically significant (95% level or above) and that the *para* effect of the 5-substituent in IV is not important. However, the value of p$K_a{}^\circ$ (the intercept) of −0.296 in eq 1 is increased to −0.251 in eq 2, the latter more closely approaching the experimentally measured value of −0.23 for no. 2 in Table I. The use of σ_R[9] or $\sigma_R{}'$[10] in place of $\sigma_p{}^+$ gave no improvement over that represented by eq 2.

The data in Table I show that all six IVa's are slightly stronger acids in 10 volume % aqueous ethanol than they are in water. As shown by eq 3 for IVa,

$$\begin{array}{lcccc} \mathrm{p}K_a = -0.414 - 3.00\sigma_m & \overset{r}{-0.998} & \overset{s}{0.056} & 100.0\% & (3) \end{array}$$

there is also an excellent correlation between pK_a in 10 vol % aqueous ethanol and σ_m. The ρ_m values of −3.10 and −3.00 in eq 1 and 3 are in fairly close agreement and thus it appears that the acid-strengthening effect of ethanol on IVa is more or less constant throughout the series, *i.e.*, the effect lies mainly in the difference between the intercepts of −0.296 and −0.414 in eq 1 and 3.

Whereas good correlations exist between ν_b and ν_a for I[3] and for II,[4] there is no significant correlation between ν_b and ν_a for III[5] or for those reported in Table I for IV. For all four of these series, the reported ν values were calculated from the longest observed wavelength maxima. The ν_b and ν_a values for series I and II are for corresponding ^1L_b bands while those for series III and IV are not. The ν_b values reported for III[5] and IV are for ^1L_b bands while the ν_a values are for ^1L_a bands. In another study,[11] ν_b values for the ^1L_a bands of series III and IV were determined. These values are recorded in Table II along with ν_a and ν_b values for the ^1L_a bands of I and II. Using these data as shown in eq 4 and 5, statistically significant correlations exist between ν_b and ν_a for III and

$$\nu_b \text{ (for IIIb)} = 16{,}011 + 0.526\nu_a \text{ (for IIIa)} \qquad (4)$$

$$\overset{r}{0.975} \quad \overset{s}{271} \quad 100.0\%$$

$$\nu_b \text{ (for IVb)} = 17{,}674 + 0.470\nu_a \text{ (for IVa)} \qquad (5)$$

$$\overset{r}{0.944} \quad \overset{s}{273} \quad 98.4\%$$

between ν_b and ν_a for IV. For I and II, there are no significant correlations between ν_b and ν_a for the ^1L_a bands.

For I,[3] fairly good correlations exist between ν_a or ν_b and $\sigma_p{}^+$ constants, whereas for II[4] there is no significant correlation between either of these variables and σ_m. Similarly, for III,[5] fairly good correlations exist between ν_a or ν_b and σ_p,[7] whereas for IV there is no significant correlation between either of these variables and σ_m. The failure of such correlations for series II and IV may be due in part to the operation of a large "area" effect.[3] That is, the substituent affects not only the reaction site, but the entire molecule since the spectral "reaction" encompasses the entire molecule. The failure of such correlations have also been reported for a series of 5-substituted 3-nitroanilines.[12]

For II,[4] very good correlations exist between $\Delta\nu_a{}^*$ or $\Delta\nu_b{}^*$ and $(\sigma_p{}^\pm - \sigma_m)$, where $\Delta\nu_a{}^* = (\nu_a$ for IIa minus ν_a for the corresponding Ia), $\Delta\nu_b{}^* = (\nu_b$ for IIb minus ν_b for the corresponding Ib), and $\sigma_p{}^\pm$ is the $\sigma_p{}^+$ or the $\sigma_p{}^-$ [7] value as applicable. In these correlations data for the 4-nitro compounds were not in-

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[8] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

[9] R. W. Taft, Jr., *ibid.*, **79**, 1045 (1957).

[10] L. A. Cohen and W. M. Jones, *ibid.*, **85**, 3402 (1963).

[11] J. P. Idoux, Ph.D. Dissertation, Texas A & M University, College Station, Tex., August 1966.

[12] J. P. Idoux and C. K. Hancock, *J. Org. Chem.*, **32**, 1935 (1967).

TABLE II

ACIDIC AND BASIC WAVE NUMBERS FOR THE ^1L_a BANDS OF SERIES I AND II AND BASIC WAVE NUMBERS FOR THE ^1L_a BANDS OF SERIES III AND IV

	Series					
	I, cm^{-1}		II, cm^{-1}		III, cm^{-1}	IV, cm^{-1}
Substituent	$\nu_a \times 10^{-4}$	$\nu_b \times 10^{-4}$	$\nu_a \times 10^{-4}$	$\nu_b \times 10^{-4}$	$\nu_b \times 10^{-4}$	$\nu_b \times 10^{-4}$
OCH_3	3.57	3.55	4.29	3.16	3.51	
CH_3	3.56	3.52	3.41	3.41	3.51	3.38
$NHCOCH_3$	4.18	4.04		3.29		
H	3.60	3.56	3.60	3.56	3.54	3.54
C_6H_5	3.94	3.64				
Cl	3.68	3.79	3.50	3.48		3.47
CO_2CH_3	4.15	3.82	3.66	3.50		
$COCH_3$	3.92	3.26				
NO_2			3.66	3.53	3.85	3.55
CHO			3.61	3.53		
OC_4H_9					3.52	
F					3.61	
Br					3.62	3.43
CF_3					3.68	

cluded because ν_b and ν_a for 4-NO_2-I were not available. For IV, when values for the 4-nitro substituent are included, no significant correlations exist between $\Delta\nu_a^*$ or $\Delta\nu_b^*$ and $(\sigma_p^{\pm} - \sigma_m)$, where $\Delta\nu_a^* = (\nu_a$ for IVa minus ν_a for the corresponding IIIa) and $\Delta\nu_b^* = (\nu_b$ for IVb minus ν_b for the corresponding IIIb), all ν values being for corresponding ^1L_a bands. If the values for the 4-nitro substituent are omitted, correlation of $\Delta\nu_b^*$ or $\Delta\nu_a^*$ with $(\sigma_p^{\pm} - \sigma_m)$ gives eq 6 and 7. Eq 6 and 7 show that as the resonance electron-donating properties of the substituent increase [*i.e.*, $(\sigma_p^{\pm} - \sigma_m)$ becomes more negative], $\Delta\nu_b^*$ becomes increasingly positive, and $\Delta\nu_a^*$ becomes increasingly negative. Thus, eq 6 and 7 indicate that the meaning of the substituent parameter $(\sigma_p^{\pm} - \sigma_m)$ as interpreted previously[4] (*i.e.*, as being an approximate measure of the maximum resonance contribution that any substituent can make in I, II, III, or IV) is correct.

$$\Delta\nu_b^* = 202 - 2912\,(\sigma_p^{\pm} - \sigma_m) \quad \overset{r}{-0.986} \quad \overset{s}{193} \quad 99.8\% \qquad (6)$$

$$\Delta\nu_a^* = -514 + 5853\,(\sigma_p^{\pm} - \sigma_m) \quad \overset{r}{0.978} \quad \overset{s}{485} \quad 99.6\% \qquad (7)$$

Correlations between Isoelectronic Series.—It can be seen that Ia is isoelectronic with IIIb as is IIa with IVb. Accordingly, it seemed of interest to compare the spectral data for these two pairs of series of compounds. Equations 8 and 9 show that there are good correlations between ν_a for Ia and ν_b for IIIb and between ν_a for IIa and ν_b for IVb. The ν values used in eq 8 and 9 are for corresponding ^1L_b bands. Similarly good correlations for corresponding ^1L_a bands are shown in eq 10 and 11. Correlations of noncorresponding bands gave poor results in all cases.

$$(\nu_a \text{ for Ia}) = -7840 + 1.50(\nu_b \text{ for IIIb}) \quad \overset{r}{0.984} \quad \overset{s}{285} \quad 100.0\% \qquad (8)$$

$$(\nu_a \text{ for IIa}) = 10{,}900 + 0.733\,(\nu_b \text{ for IVb}) \quad \overset{r}{0.948} \quad \overset{s}{244} \quad 98.6\% \qquad (9)$$

$$(\nu_a \text{ for Ia}) = -1088 + 1.05(\nu_b \text{ for IIIb}) \quad \overset{r}{0.996} \quad \overset{s}{64} \quad 99.6\% \qquad (10)$$

$$(\nu_a \text{ for IIa}) = -13{,}191 + 1.40(\nu_b \text{ for IVb}) \quad \overset{r}{0.976} \quad \overset{s}{302} \quad 97.6\% \qquad (11)$$

Experimental Section

5-Substituted 2-Nitroanilines.—*o*-Nitroaniline was obtained commercially. 5-Methyl and 5-methoxy 2-nitroanilines were prepared from *m*-toluidine and *m*-anisidine by acetylation, nitration, hydrolysis, steam distillation, and recrystallization from aqueous ethanol. The other three compounds used in this study were prepared as indicated by footnotes to Table III.

TABLE III

MELTING POINTS OF 5-SUBSTITUTED 2-NITROANILINES

5-Substituent	Mp, °C[a]	Lit. mp, °C
CH_3	109.5–110.5	109[b]
H	71–72.2	71.5[c,d]
OCH_3	128–129.5	131[e]
Cl	124.5–125.5	124–125[f]
Br	151.5–152.5	151–152[g,h]
NO_2	135–136	136[i]

[a] Corrected. [b] A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **103**, 897 (1913). [c] I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1953, p 628. [d] Obtained commercially. [e] R. Meldola and F. G. C. Stephens, *J. Chem. Soc.*, **89**, 923 (1906). [f] F. K. Beilstein, "Handbuch der organischen Chemie," Vol. 12, 4th ed, Springer-Verlag, Berlin, West Germany, 1929, p 730. [g] See ref *f*, Vol. 12, 2nd Suppl, p 402. [h] H. A. Mayes and E. E. Turner, *J. Chem. Soc.*, 691 (1928). [i] K. H. Pausacker and J. G. Scroggie, *ibid.*, 1897 (1955).

Ultraviolet Spectral Studies and Measurement of pK_a Values of 5-Substituted 2-Nitroanilines.—The ultraviolet spectra were measured and the pK_a's were calculated as described previously.[5] The resulting data are shown in Table I. The pK_a's were also obtained in 10 vol % aqueous ethanol and the results are shown in parentheses in Table I. The average deviation from the mean of quadruplicate pK_a's for each compound exceeded 0.02 only in the cases of 0.03 for the 5-bromo and 5-nitro compounds in 10 vol % aqueous ethanol and of 0.04 for the 5-nitro compound in water.

Acknowledgments.—This study was supported in part by a research grant from the Robert A. Welch Foundation. Helpful suggestions of Dr. E. A. Meyers and Dr. J. O. Schreck are gratefully acknowledged. The statistical calculations were performed by the Data Processing Center, Texas Engineering Experiment Station, College Station, Tex., on an IBM-7094 computer.