amine also affects the rate of the biological dealkylation.[25] Diffusion to the enzyme site may be rate limiting and not the dealkylation reaction.

It has been argued that the N-oxide is not an intermediate in the biological dealkylation of tertiary amines because morphine is demethylated by rat liver microsomes 1.4 times more rapidly than N-trideuteriomorphine.[24,26] It was assumed that these data reflect a primary isotope effect and that cleavage of a proton adjacent to nitrogen is rate limiting. Essentially the same isotope effect (1.3) was observed in the oxidation of trimethylamine with chlorine dioxide (equations 16–18), a reaction which is known to proceed by electron abstraction from nitrogen and not by α-hydrogen abstraction.[21] It could be that a secondary isotope effect is being observed in the demethylation of morphine with the rate-limiting step being electron abstraction or N-oxide rearrangment. More work is required to decide this point.

Registry No.—Bu_3N N-oxide, 7529-21-7; *t*-$BuNMe_2$ N-oxide, 17061-11-9; *t*-$BuNMe_2$ N-oxide picrate, 17061-12-0; $PhCH_2NMe_2$ N-oxide, 5400-82-8; $(PhCH_2)_2NMe$ N-oxide picrate, 17072-69-4; $(PhCH_2)_3N$ N-oxide picrate, 17061-05-1; N-methylpiperidine N-oxide picrate, 17061-06-2; $PhNMe_2$ N-oxide picrate, 17061-07-3; 4-picoline N-oxide picrate, 17061-08-4.

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[25] R. E. McMahon, *J. Med. Pharm. Chem.*, **4**, 67 (1961).

[26] C. Elison, W. H. Elliott, M. Lock, and H. Rapoport, *J. Med. Chem.*, **6**, 237 (1963).

Structure–Acidity and Structure–Electronic Spectral Studies of Some Substituted Nitroanilines[1a]

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The pK_a's and electronic spectra of seven 3-substituted 4-nitroanilines have been measured. A good correlation was obtained between the pK_a's and σ_m. The reaction constant for this series does not conform to that required by the additivity principle for the effect of a constant substituent. Reaction constants for correlations between pK_a's and substituent constants for a series of 4-substituted 2-nitroanilines and a series of 5-substituted 2-nitroanilines also do not conform to that required by the additivity principle. The deviations for these three series are discussed in terms of variation in resonance interaction between the constant nitro groups and the reaction site amino groups. The reaction constants for the above three series are compared with those for a series of 5-substituted 3-nitroanilines and a series of 4-substituted 3-nitroanilines. No significant results were obtained for correlations involving any of the spectral data. The excited-state pK_a*'s have been calculated for a series of 4-substituted 2-nitroanilines and for a series of 5-substituted 2-nitroanilines. The pK_a*'s for both series correlate fairly well with $\sigma_p{}^+$. They give good correlations when $\sigma_p\pm$ is used. The excited-state reaction constants for the two series are significantly different. Jaffé's assumption that in excited states *meta*- and *para*-substituted compounds are correlated by lines of different slope appears to be valid for the 4- and 5-substituted 2-nitroanilines.

Successful structure–acidity correlations and, for some of the series, structure–electronic spectral correlations have been reported for the following series of organic compounds: 4-substituted 2-nitrophenols,[3] 5-substituted 2-nitrophenols,[4] 4-substituted 2-chlorophenols,[5] 4-substituted 2-nitroanilines (III, see Chart I),[6] 5-substituted 2-nitroanilines (IV),[7] and 5-substituted 3-nitroanilines (I).[8] The pK_a's for a series of 4-substituted 3-nitroanilines (VI) have also been reported.[9] These studies have been extended to a series of 3-substituted 4-nitroanilines (II), and the resulting data along with the data for I, III, IV, and VI allow a comparison of the different substituent effects on the electronic spectra and acidities.

Jaffé and Jones[10] have reported correlations between excited-state pK*'s and substituent constants for several different series of aromatic acids and bases. They suggested that (1) in excited states *meta* substituents may enter into direct resonance interaction with a side chain and (2) *meta*- and *para*-substituted compounds may fall on different correlation lines, *i.e.*, they may require different reaction constants. An investigation of the first of these suggestions has been reported previously.[8] A study of the pK_a*'s of III and IV allows an investigation of the second suggestion.

Results and Discussion

Correlation of the pK_a's and Electronic Spectra of 3-Substituted 4-Nitroanilines (II) with Substituent Constants and Comparison with Correlations for Series I, III, IV, and VI.—For a series of 4-substituted 2-nitroanilines (III),[6] a good quantitative relationship exists between the pK_a's and σ_p.[11a] A similar relationship exists between pK_a and σ_m[11a] for a series of 5-substituted 2-nitroanilines (IV).[7] However, the Hammett ρ values[12a] of -3.23 for III and -3.10 for IV do not conform to that required by the additivity principle[11b] for a constant *ortho* substituent, since both are significantly more negative than that predicted by the

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[1] (a) Abstracted in part from the Ph.D. Dissertation of J. P. I., Texas A & M University, Aug 1966; (b) National Aeronautics and Space Administration Fellow, 1963–1966.

[2] To whom inquiries should be addressed.

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

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

[7] C. K. Hancock, R. A. Brown, and J. P. Idoux, *ibid.*, **33**, 1947 (1968).

[8] J. P. Idoux and C. K. Hancock, *ibid.*, **32**, 1935 (1967).

[9] A. R. Lawrence and L. N. Ferguson, *ibid.*, **25**, 1220 (1960).

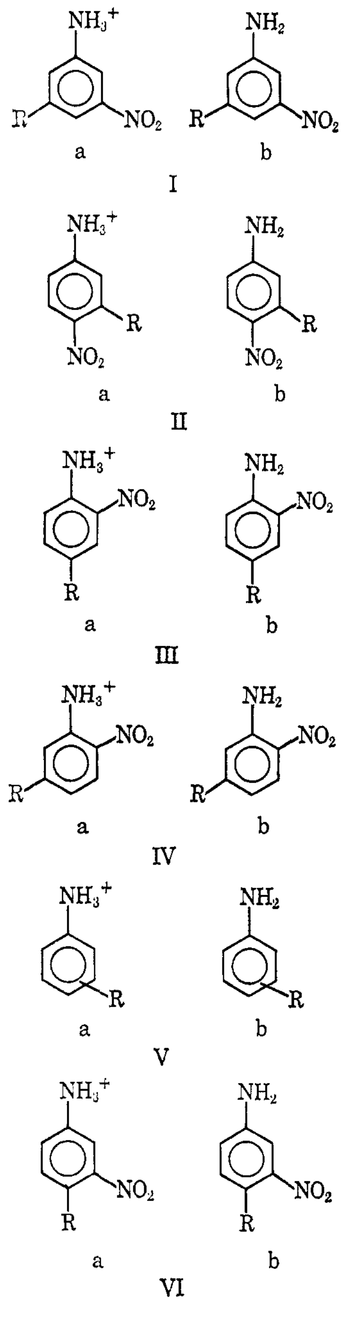
[10] H. H. Jaffé and H. L. Jones, *ibid.*, **30**, 964 (1965).

[11] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953): (a) p 222; (b) p 246; (c) Table I, reaction no. 26a, p 200.

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

CHART I

ACIDIC (a) AND BASIC (b) SPECIES FOR SUBSTITUTED ANILINES



ρ value of −2.77 found[11c] for a series of *meta*- and *para*-substituted anilines (V). In III and IV, the nitro group can affect the amino group by a combination of polar, resonance, steric, and intramolecular hydrogen-bonding effects. It was thought desirable to extend the scope of the above studies to a series of substituted nitroanilines in which the nitro group affects the amino group only by polar and resonance effects. Such a series is the 3-substituted 4-nitroanilines (II). The pK_a's and absorption spectra of II have been measured and are recorded in Table I.

TABLE I

ACIDITY AND SPECTRAL DATA FOR 3-SUBSTITUTED 4-NITROANILINES

3 substituent	pK_a	$\lambda_b{}^a$	$\nu_b{}^b \times 10^{-4}$	$\epsilon_b{}^c \times 10^{-3}$	$\lambda_a{}^d$	$\nu_a{}^e \times 10^{-4}$	$\epsilon_a{}^f \times 10^{-3}$
H	1.02[g]	380[h]	2.63	12.98	259	3.86	8.19
CF_3	−0.05	380[i]	2.63	10.07	237.5[j]	4.21	4.72
Cl	0.26	376.5[k]	2.66	10.42	253[l]	3.95	4.24
$COCH_3$	−0.14	388.5	2.57	14.06	258	3.87	6.19
NO_2	−1.20	386	2.59	11.17	...	...	...
$CO_2C_2H_5$	−0.11	382[m]	2.62	12.54	250[n]	4.00	4.80
CH_3	1.41[o]	379	2.64	11.38	256	3.91	5.76

[a] λ_b (mμ) = λ_{max}^{NaOH}. [b] ν_b (cm^{-1}) = $(1/\lambda_b \times 10^7)$. [c] ϵ_b = extinction coefficient in basic solution. [d] λ_a (mμ) = λ_{max}^{HCl}. [e] ν_a (cm^{-1}) = $(1/\lambda_a \times 10^7)$. [f] ϵ_a = extinction coefficient in acidic solution. [g] M. Kilpatrick and C. A. Arenberg, *J. Amer. Chem. Soc.*, **75**, 3812 (1953), report a thermodynamic pK_a of 0.98. [h] There is an inflection at 226 mμ (ϵ 6103). [i] There is another peak at 230 mμ (ϵ_{max} 7053). H. H. Szmant and J. F. Anzenberger, *J. Amer. Chem. Soc.*, **76**, 3785 (1954), report λ_{max} 370 mμ (ϵ_{max} 11,600) and λ_{max} 234.5 mμ (ϵ_{max} 7420), both in 95% equeous ethanol. [j] This is a shoulder; ref *i* reports λ_{max} 245 mμ (ϵ_{max} 4940) for 10 *M* alcoholic HCl. [k] There is an inflection at 256.5 mμ and a plateau at 230.5 mμ. [l] There is an inflection at 295 mμ. [m] There is a shoulder at 257 mμ. [n] This is a shoulder. [o] pK_a reported as 1.58 by H. C. Brown, D. N. McDaniel, and O. Häfliger in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press Inc., New York, N. Y., 1955, p 594.

$$\text{p}K_a = 1.12 - 3.13\,\sigma_m, \quad \overset{r}{-0.974}, \quad \overset{s}{0.21}, \quad 99.9\% \qquad (1)$$

For II, a good correlation[13a,14] has been obtained between the pK_a's and σ_m as indicated in eq 1. The ρ value of −3.13 in eq 1 is significantly more negative than predicted by the additivity principle and in fact is very similar to the ρ values for III and IV. This means that the electrical effects of the substituents are more effectively transmitted to the reaction sites in II, III, and IV than in V. One would expect some deviation in ρ from that predicted by the additivity principle whenever there exists a significant interaction between the constant substituent and the reaction site. The deviations of the ρ values for III and IV from that for V might arise owing to variations in steric or intramolecular hydrogen-bonding interactions between the constant nitro group and the amino group. However, as noted above, the ρ value for II, where these latter interactions are not possible, is very similar to the ρ values for III and IV. This indicates that the latter interactions are not significantly important in causing the deviations of the ρ values. Also, for a series of 5-substituted 3-nitroanilines (I)[8] and for a series of 4-substituted 3-nitroanilines (VI)[9] the ρ values of −2.87 and −2.83 are close to that of −2.77 predicted by the additivity principle. In both I and VI, the only direct effect of the nitro group on the reaction site is an inductive one. Thus, it appears that the inductive effect of the constant nitro group does not significantly affect the reaction constant. The variable effect on the reaction site of the constant nitro group in II, III, and IV which causes the deviations of the ρ's from the predicted value appears to be due to variation in resonance interaction between the constant nitro group and the reaction site amino group. This variation in resonance interaction arises because of the different electron demands of the various substituents.

In an attempt to obtain a more significant relation and perhaps account for the deviation of the ρ value,

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

[14] In the equations throughout this paper, *r* is the linear correlation coefficient and *s* is the standard deviation from regression. The percentage value given at the end of each equation is the percentage confidence level as determined by the Student "*t*" test.[13b]

the pK_a's of II were correlated with $\sigma_m{}^+$,[15] $\sigma_p{}^+$,[15] or σ_R.[16] However, in no case was there any correlation more significant than that reported in eq 1. Similar correlations were carried out on III and IV. No correlations more significant than originally reported[6,7] were obtained.

For II, there is no significant correlation between ν_b and ν_a, ν_b and σ_m, ν_a and σ_m, $\Delta\nu$ (where $\Delta\nu = \nu_b - \nu_a$) and pK_a, or $\Delta\nu$ and σ_m.

The negative values for the ρ's of series I, II, III, IV, and VI indicate that an electron-withdrawing substituent increases the acidity of a substituted nitroanilinium ion relative to the respective unsubstituted nitroanilinium ion and this is observed in every case. In general, it has been observed that the acid strengths of the substituted nitroanilinium ions decrease in the following order: III > IV > II > I > VI. It has been pointed out[17] that substitution in benzenes does not produce great changes or new bands in the uv spectra, but only modifies the spectrum of the parent compound. Perturbation resulting from the introduction of a substituent causes shifts in absorption bands and changes in intensity of these bands. An examination of Table I shows that for λ_b of II, relative to *p*-nitroaniline, electron-donating groups and halogens cause blue shifts (*i.e.*, shifts to shorter wavelengths) while electron-withdrawing groups cause red shifts (*i.e.*, shifts to longer wavelengths). This same order has been observed for λ_b of I[8] relative to *m*-nitroaniline. The same relationship has also been observed for λ_b of IV,[7] but the opposite order is observed for λ_b of III,[6] both relative to *o*-nitroaniline. For VI, if R = F or OCH_3, a red shift is observed while a blue shift is observed if R = Cl. No change was observed when the 4 substituent was Br or CH_3.[18]

For I, III, and IV, where $\lambda_b{}'$ values (^1L_a bands) were found, it was observed that, in general, electron-donating groups and halogens cause red shifts (for III, halogens cause blue shifts) while electron-withdrawing groups cause blue shifts. For these same three series, λ_a is affected in the same way by substituents as is $\lambda_b{}'$.

Correlation of the Excited-State pK_a*'s of Some 4-Substituted 2-Nitroanilines (III) and Some 5-Substituted 2-Nitroanilines (IV) with Substituent Constants.—Jaffé and coworkers[10,19] have outlined a method for calculating pK*'s which only requires measurement of the absorption frequency of the basic and acidic forms of the compounds under study. The method depends on the Förster[20] cycle and may be applied to absorption spectra measurements provided pairs of corresponding states can be found. The wavenumbers in acidic solution for a series of 4-substituted 2-nitroanilines (III) and for a series of 5-substituted 2-nitroanilines (IV) have been reported previously.[6,7] The spectra of IIIa and IVa would be expected to resemble the spectra of the 3-substituted nitrobenzenes and the spectra of the 4-substituted nitrobenzenes, respectively.[17] Previous reports[21] for the ^1L_a bands of the 3-substituted nitrobenzenes and the 4-substituted nitrobenzenes correspond very closely to those reported for IIIa[6] and IVa[7] and the latter bands are therefore classified as ^1L_a bands. The ^1L_a bands in basic solution for III and IV have also been reported previously.[7]

The pK_a*'s for III ($pK_a{}^{*III}$) and IV ($pK_a{}^{*IV}$), calculated from the ν values for the ^1L_a bands, are recorded in Table II. The relationships between $pK_a{}^{*III}$ and σ_p, $\sigma_p{}^+$, or $\sigma_p{}^\pm$ ($\sigma_p{}^\pm$ is the $\sigma_p{}^+$ or the $\sigma_p{}^-$ value, whichever is applicable) are shown in eq 2–4 while those for $pK_a{}^{*IV}$ and σ_m, $\sigma_m{}^+$, or $\sigma_p{}^\pm$ are shown in eq 5–7. Equations 4 and 7 are statistically significant and their ρ values of −5.24 and −3.27 are significantly different; *i.e.*, the ranges of ($\rho \pm s_\rho$) for the two equations do not overlap (s_ρ is the standard error of ρ). Even though eq 5 is not statistically significant, the ρ values

TABLE II

pK_a*'s FOR 4-SUBSTITUTED 2-NITROANILINES (III) AND 5-SUBSTITUTED 2-NITROANILINES (IV)

Substituent	$pK_a{}^{*III}$	$pK_a{}^{*IV}$
OC_4H_9	−1.40	...
OCH_3	−2.05	...
CH_3	−2.96	−2.56
H	−4.86	−4.86
F	−5.08	...
Br	−3.75	−3.38
Cl	...	−3.15
CF_3	−7.39	...
NO_2	−13.28	−7.86

$$\begin{array}{lll} & \quad r,\ s,\ s_\rho & \\ pK_a{}^{*III} = -4.13 - 8.99\sigma_p, & -0.925, 1.56, 1.50, 99.9\% & (2) \\ pK_a{}^{*III} = -5.28 - 6.15\sigma_p{}^+, & -0.866, 2.07, 1.58, 98.8\% & (3) \\ pK_a{}^{*III} = -4.88 - 5.24\sigma_p{}^\pm, & -0.936, 1.45, 0.88, 99.8\% & (4) \end{array}$$

$$\begin{array}{lll} & \quad r,\ s,\ s_\rho & \\ pK_a{}^{*IV} = -3.12 - 4.38\sigma_m, & -0.656, 1.85, 2.90, 77.1\% & (5) \\ pK_a{}^{*IV} = -3.17 - 4.19\sigma_m{}^+, & -0.608, 1.95, 3.15, 72.4\% & (6) \\ pK_a{}^{*IV} = -3.56 - 3.27\sigma_p{}^\pm, & -0.923, 0.95, 0.79, 97.4\% & (7) \end{array}$$

of −8.99 and −4.38 for eq 2 and 5 are significantly different by the same test as that for the ρ values of eq 4 and 7. Of eq 2–7, the least significant is eq 6 and the ρ values for eq 3 and 6 are not significantly different. Thus, in two of three cases, it appears that Jaffé's assumption that in excited states *meta*- and *para*-substituted compounds are correlated by lines of different slope is valid for III and IV. It is also of interest that the exalted substituent parameter, $\sigma_p{}^\pm$, gives the best correlations for both series. It is particularly significant that the pK_a*'s of IV, where the 5 substituent is *meta* to the reaction center amino group, correlate best with the exalted substituent constants. Neither III nor IV correlates significantly with σ_I.[16,22,23] However, series IV correlates significantly with σ_R while series III correlates significantly with $\sigma_R{}'$.[24]

For correlations involving pK_a*'s of III and IV, the resonance effect, and not the inductive effect, is of

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

(16) R. W. Taft, Jr., *ibid.*, **79**, 1045 (1957).

(17) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 12.

(18) Data not published in ref 9 were kindly provided by Dr. L. N. Ferguson.

(19) H. H. Jaffé, D. L. Beveridge, and H. L. Jones, *J. Amer. Chem. Soc.*, **86**, 2932 (1964).

(20) A. Weller, *Progr. Reaction Kinetics*, **1**, 187 (1961).

(21) W. F. Forbes, *Can. J. Chem.*, **36**, 1350 (1958).

(22) I. C. Lewis and R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **80**, 2436 (1958).

(23) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

(24) L. A. Cohen and W. M. Jones, *J. Amer. Chem. Soc.*, **85**, 3402 (1963).

primary importance, these considerations being opposite to those previously reported[8] for I.

Experimental Section

Materials.—The 3-substituted 4-nitroanilines which were commercially unavailable were prepared as indicated by footnotes to Table III.

TABLE III

MELTING POINTS OF 3-SUBSTITUTED 4-NITROANILINES

3 substituent	Mp, °C[a]	Lit, mp, °C
H	146–147.5	145–147[b]
CF_3	127–128.5	129[c]
Cl	156–157	156–157[d]
CH_3CO	148–150	148–149,[e] 150[f]
NO_2	153–155[g]	154[h]
$CO_2C_2H_5$	105–107	107.5[i,j]
CH_3	134.5–135.5	135[k,l]

[a] Corrected. [b] F. K. Beilstein, "Handbuch der organischen Chemie," Vol. XII, 4th ed, J. Springer, Berlin, 1929, p 711. F. K. Beilstein, "Handbuch der organischen Chemie," Vol. XII, 1950, p 477 (2nd supplement). [d] H. H. Hodgson and A. Kershaw, *J. Chem. Soc.*, 2919 (1929). [e] J. C. E. Simpson, C. M. Atkinson, K. Schofield, and O. Stephenson, *ibid.*, 654 (1945). [f] W. A. Waters, *ibid.*, 629 (1945). [g] A benzene solution of the substance melting between 153 and 155° was chromatographed on alumina according to K. Pausaika and J. Scroggie, *ibid.*, 1897 (1955). Only one band was observed. [h] O. N. Witt and E. Witte, *Ber.*, **41**, 3091 (1908). [i] L. Kalb and O. Gross, *ibid.*, **59**, 736 (1926). [j] *Chem. Zentr.*, II, 951 (1899). [k] J. W. Cook and O. L. Brady, *J. Chem. Soc.*, **117**, 752 (1920). [l] J. P. Wibaut, *Rec. Trav. Chim.*, **32**, 287 (1913).

Analytical grade hydrochloric acid was used in the spectral studies. All water used was deionized by passing distilled water through an "Ilco-Way" universal deionizing column.[25]

Ultraviolet Spectra and Measurement of pK_a's.—Stock solutions (0.0003 *M*) were prepared as described previously.[8] The absorption spectra were measured as described previously,[8] except that hydrochloric acid solutions of various concentrations, rather than buffered solutions, were used. The pK_a's were calculated from eq 8.[12b] In eq 8, *A* is the absorbance of the

$$\mathrm{p}K_a = H_0 - \log \frac{A - A_a}{A_b - A} \tag{8}$$

solution containing various concentrations of aqueous hydrochloric acid, A_a is the absorbance of the solution in concentrated hydrochloric acid, A_b is the absorbance of the solution in 0.2 *M* sodium hydroxide, and H_0 is the acidity function for hydrochloric acid.[26]

The medium shift was minimal in all cases and the absorbance of all solutions was measured at the wavelength at which A_b was measured.

Calculation of the Excited-State pK_a*'s.—The pK_a*'s were calculated using eq 9.[10,19] In eq 9, ν_b and ν_a represent the frequencies of corresponding transitions in wavenumbers of a base and its conjugate acid, *N* is Avogadro's constant, *h* is Planck's constant, *c* is the velocity of light, and *R* is the gas constant. The uncertainty involved in the calculation of pK_a^+ has been treated elsewhere.[10]

$$\mathrm{p}K_a{}^* = \frac{(\nu_b - \nu_a)Nhc}{2.303RT} + \mathrm{p}K_a \tag{9}$$

Registry No.—IIb (R = H), 100-01-6; IIb (R = CF_3), 393-11-3; IIb (R = Cl), 825-41-2; IIb (R = $COCH_3$), 16994-13-1; IIb (R = NO_2), 610-41-3; IIb (R = $CO_2C_2H_5$), 16994-15-3; IIb (R = CH_3), 611-05-2.

Acknowledgments.—This study was supported in part by a research grant from The Robert A. Welch Foundation. The statistical calculations were performed by the Data Processing Center, Texas Engineering Experiment Station, College Station, Texas, on an IBM-7094 computer.

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[25] Illinois Water Treatment Co., Rockford, Ill.

[26] E. M. Arnett and George W. Mach, *J. Amer. Chem. Soc.*, **88**, 1177 (1966).

Liquid Crystals. II.[1] Effects of Terminal Group Substitution on the Mesomorphic Behavior of Some Benzylideneanilines

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In an effort to prepare nematic compounds with crystal–nematic transition temperatures below 100°, benzylideneaniline was substituted with a variety of functional groups in the *para* positions of both rings. Of the 21 new compounds that were prepared by the acid-catalyzed condensation of appropriate *para*-substituted benzaldehydes with *para*-substituted anilines only nine exhibited nematic behavior. Trends in the mesomorphic behavior of a homologous series, namely, *p*-*n*-alkoxybenzylidene-*p*′-aminoacetophenones, are discussed in detail. The profound effect of changes in the nature of terminal groups on the probability of mesomorphism in benzylideneanils is demonstrated by comparison with *para*-substituted benzylidene-*p*′-aminobiphenyl derivatives. That some residual lateral intermolecular attractions are necessary in order to maintain nematic order is demonstrated by the fact that substitution of groups with dipoles acting along the long axis of the molecule destroys mesomorphic behavior. Replacement of oxygen by sulfur in the alkoxy group of benzyldeneanils results in loss of mesomorphic (enantiotropic) behavior.

Liquid crystallinity or mesomorphism[2] is a unique state of matter intermediate between a crystalline solid and a normal isotropic liquid. The phenomenon is usually exhibited by long, rod-shaped molecules which contain dipolar groups. This permits the molecules to orient themselves with their long axes parallel. Since rotation can occur only about the long axis of the molecule, compounds of this type behave as anisotropic liquids and are birefringent. Three main types of mesomorphic states have been recognized:[3] nematic mesophases, in which the molecules can rotate only about their long axes; smectic mesophases, in which the

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[1] For the first paper in this series, see J. Goldmacher and L. Barton, *J. Org. Chem.*, **32**, 476 (1967).

[2] G. Friedel, *Ann. Phys.* (Paris), **18**, 273 (1922).

[3] G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962, Chapters I, VIII, and IX.