

Appendix

The radical-stabilizing ability of all substituents may be understood in terms of a crude Hückel MO model. The substituted benzyl radical will be approximated by $\ddot{X}-CH_2\cdot$ or $Y-CH_2\cdot$. More realistic models, a benzyl radical with either a changed Coulomb integral for the *para* carbon or a *para* substituent which contributes an extra π -orbital to the system, treated by second-order perturbation methods, lead to similar results. The parameters for an electron-donating substituent, X, are $\alpha_X = \alpha_0 + h\beta_0$, $\beta_{CX} = k\beta_0$, with the substituent contributing two π -electrons. The parameters for an electron-withdrawing substituent, Y, are $\alpha_Y = \alpha_0 - h\beta_0$, $\beta_{CY} = k\beta_0$, with the substituent contributing a vacant p-orbital. As defined here, $h \geq 0$ and $k > 0$. In Table III, we compare the change in π -energy (D.E.) for the bonding of both types of substituents with a carbonium ion, radical, and carbanion carbon. For parameters as defined, the electron-donating substituent always stabilizes a carbonium ion and the electron-withdrawing group stabilizes an anion, but both types of groups stabilize a radical by an amount $(-h + [h^2 + 4k^2]^{1/2})/2$. Of course, this model does not allow for electron-repulsion effects nor does it allow for the use of an empty d-

orbital of an electron-donating substituent in addition to its filled p-orbital, a factor which is undoubtedly responsible for placing the methylthio group so far off a correlation diagram which considers only polar effects. This crude model should not be pushed so far as to require a V-shaped or parabolic σ - ρ plot for radical reactions (although Klopman's⁶ is quite close to parabolic, and the relative reactivities²⁸ of substituted styrenes in copolymerization, to produce a substituted benzyl radical, correlate with σ to exhibit a slight, but noticeable, upward curvature), but is intended to suggest that an apparent correlation with σ^+ may result, not necessarily only because of a resemblance of the transition state to a benzyl cation, but also because of the special nature of substituent effects on benzyl radical stabilities.

TABLE III
SUBSTITUENT EFFECTS ON HMO DELOCALIZATION ENERGIES

Electron-donating		Electron-withdrawing	
n_π System	D.E./ β	n_π System	D.E./ β
2 Cation	$-h + \sqrt{h^2 + 4k^2}$	0 Cation	0
3 Radical	$(-h + \sqrt{h^2 + 4k^2})/2$	1 Radical	$(-h + \sqrt{h^2 + 4k^2})/2$
4 Anion	0	2 Anion	$-h + \sqrt{h^2 + 4k^2}$

(28) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Fig. 4.9, p. 137.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF TEXAS A&M UNIVERSITY, COLLEGE STATION, TEXAS]

The Correlation of the Electronic Spectra and Acidity of 5-Substituted 2-Nitrophenols with Structure

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RECEIVED MAY 18, 1964

The electronic spectra and pK_A 's of a series of 5-substituted 2-nitrophenols (I) have been measured and compared with corresponding data previously reported (ref. 6) for a series of 4-substituted 2-nitrophenols (II). For each series, there is a good correlation between pK_A and Hammett's σ ; however, the ρ -value of -3.01 for I is much more negative than that of -2.16 for II. Whereas, for II, satisfactory correlations were found for $\Delta\nu$ vs. pK_A , ν_B vs. σ_p^+ , and ν_A vs. σ_p^+ , the corresponding correlations for I are unsatisfactory [$\nu_B = (1/\lambda_{\max}^{NaOH}) \times 10^7$, $\nu_A = (1/\lambda_{\max}^{HCl}) \times 10^7$, $\Delta\nu = \nu_B - \nu_A$]. For both series, there are good correlations between ν_B and ν_A . A good correlation between $\Delta\nu$ and σ_p^+ exists for II, but no satisfactory linear relationship for I could be found between $\Delta\nu$ and any pertinent set of substituent constants. However, good correlations exist between $\Delta\nu_A^*$ and $(\sigma_p^\pm - \sigma_m)$ and between $\Delta\nu_B^*$ and $(\sigma_p^\pm - \sigma_m)$, where $\Delta\nu_A^*$ is ν_A for a I minus ν_A for the corresponding II, $\Delta\nu_B^*$ is ν_B for a I minus ν_B for the corresponding II, and σ_p^\pm is the applicable σ_p^+ or σ_p^- value. It is proposed that the quantity $(\sigma_p^\pm - \sigma_m)$ is an approximate measure of the maximum resonance contribution that a substituent may make in either a 4- or a 5-substituted 2-nitrophenol. All of the above relationships are discussed.

Introduction

Recently, it has been shown^{2,3} for the 2,4-dinitrophenylhydrazones of carbonyl compounds that $\Delta\nu$, the wave number shift in basic solution, can be correlated with the substituent constants of Hammett^{4a} or Taft.⁵ Also, it has been shown⁶ that certain aspects of the electronic spectra of 4-substituted 2-nitrophenols conform to Hammett⁷ relationships. These observations indicate that the effects of sub-

stituents on chemical reactivity and on electronic spectra are similar.

The purpose of the present article is to report and comment upon the results produced by moving the variable substituent from the 4-position of 4-substituted 2-nitrophenols to the 5-position of 5-substituted 2-nitrophenols, while maintaining all other conditions as similar as possible to those for the former series. These two series of substituted 2-nitrophenols are appropriate for this study since the nitro group: (1) ensures that the pertinent electronic spectra will appear in the visible or near-ultraviolet region; (2) chelates with the hydroxy group, thereby suppressing molecular association; and (3) is sufficiently removed from the 4- or 5-substituent that no steric interaction occurs.

Results and Discussion

The pK_A 's and absorption spectra of a series of 5-substituted 2-nitrophenols have been measured and the re-

(1) Abstracted in part from the M.S. Thesis of A. D. H. C., Texas A&M University, Aug., 1963.

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

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

(4) H. H. Jaffé, *Chem. Rev.*, **53** (1953): (a) p. 222, (b) p. 246, (c) p. 199, reaction no. 23a, (d) p. 225.

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

(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, Chapter 7.

TABLE I
 ACIDITY AND SPECTRAL DATA FOR 5-SUBSTITUTED 2-NITROPHENOLS

5-Subst.	pK _A ^a	λ _B ^b	ν _B ^c	ε _B ^d × 10 ⁻³	λ _A ^e	ν _A ^f	ε _A ^g × 10 ⁻³	Δν ^h	σ _m ⁱ	σ _p ^{+j}
1 CH ₃ O	7.09	408	24,510	7.77	345	28,980	11.07	-4476	0.115	-0.778
2 CH ₃	7.25	420	23,810	5.40	348	28,730	4.18	-4926	-0.069	-0.311
3 CH ₃ CONH	6.71	413	24,210	6.99	353	28,330	11.21	-4116	.248 ^k	-0.600
4 H	7.13 ^l	418	23,920	4.70	350	28,570	3.28	-4648	.000	.000
5 C ₆ H ₅	6.74	422	23,700	6.64	328	30,580	14.24	-6884	.218	-0.179
6 Cl	6.05	410	24,420	6.09	342	29,240	4.48	-4820	.373	.114
7 CO ₂ CH ₃	6.15	426	23,470	5.38	356	28,090	3.79	-4616	.315	.385
8 CO ₂ C ₂ H ₅	6.11	426	23,470	5.17	358	27,930	3.61	-4459	.398	.522
9 NO ₂	5.04	442	22,620	4.34	363	27,510	3.78	-4886	.710	.778
10 F	6.07	405	24,690	5.36	341	29,330	3.82	-4635	.337	-0.073
11 CHO	6.00	436	22,930	4.79	359	27,850	3.47	-4919	.382	.216
12 COOH	356	28,090	3.41355	.265
13 COO ⁻	...	426	23,470	4.39104	.132

^a The pK_A's are apparent, average deviation from the mean = ±0.025. ^b λ_B (mμ) = λ_{max}^{NaOH}. ^c ν_B (cm.⁻¹) = (1/λ_B) × 10⁷. ^d ε_B = extinction coefficient in alkaline solution. ^e λ_A (mμ) = λ_{max}^{HCl}. ^f ν_A (cm.⁻¹) = (1/λ_A) × 10⁷. ^g ε_A = extinction coefficient in acid solution. ^h Δν (cm.⁻¹) = (ν_B - ν_A). ⁱ σ-Values for *m*-substituents; ref. 4a. ^j σ_p⁺ = electrophilic substituent constants; ref. 9. ^k H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959). ^l Ref. 6 reports pK_A = 7.08 (apparent), λ_B = 414 mμ, λ_A = 350 mμ. L. Doub and J. M. Vandenberg, *J. Am. Chem. Soc.*, **71**, 2416 (1949), report λ_B = 416 mμ, λ_A = 351 mμ; A. I. Biggs, *Trans. Faraday Soc.*, **52**, 35 (1956), reports pK_A = 7.21 (thermodynamic), λ_B = 420 mμ, λ_A = 353 mμ.

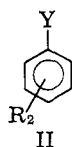
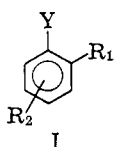
sults are shown in Table I. A good correlation exists between the pK_A's and Hammett's σ_m^{4a} constants, as illustrated in Fig. 1. Linear regression analysis^{8a} of the data in Table I gives eq. 1 with a linear correlation coefficient,

$$pK_A = 7.22 - 3.01\sigma_m \quad (1)$$

r, of -0.974 and a standard deviation from regression, *s*, of 0.16. In eq. 1, 7.22 is the regression pK_A^o value for unsubstituted 2-nitrophenol and -3.01 is ρ, the reaction constant. This equation is analogous to eq. 2 obtained previously⁶ for a series of 4-substituted 2-nitrophenols.

$$pK_A = 6.89 - 2.16\sigma_p, \quad r = -0.992, \quad s = 0.14 \quad (2)$$

In eq. 2, σ_p is Hammett's *p*-substituent constant.^{4a} In both cases, the value of ρ is negative, indicating that electron-withdrawing substituents will decrease pK_A, *i.e.*, will increase the acidity of the respective phenols. For a series of reactions of compounds with structure I, in which R₁ remains the same while R₂ is varied,



evidence has been cited^{4b} to suggest that the reaction constant is independent of the nature of R₁. On this basis, the reaction constant for compounds of structure I should be the same as the reaction constant for the same reaction of compounds of structure II. This assumption holds for the pK_A's of 4-substituted 2-nitrophenols⁶ for which ρ is -2.16, which is not significantly different from the ρ-value of -2.11 for the pK_A's of *m*- and *p*-monosubstituted phenols.^{4c} However, in the series of 5-substituted 2-nitrophenols, the reaction constant does not conform with this assumption, since it is significantly more negative than the reaction constant for *m*- and *p*-monosubstituted phenols. This means that the electronic characteristics of the substituent are transmitted more effectively to the reaction site in the 5-substituted 2-nitrophenols.

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

(9) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4980 (1958).

In order to understand this effect, some importance must be attached to the position of the variable 5-substituent which is *para* to the strongly deactivating nitro group. If the 5-substituent is of a resonance electron-releasing type, a "push-pull" effect would be

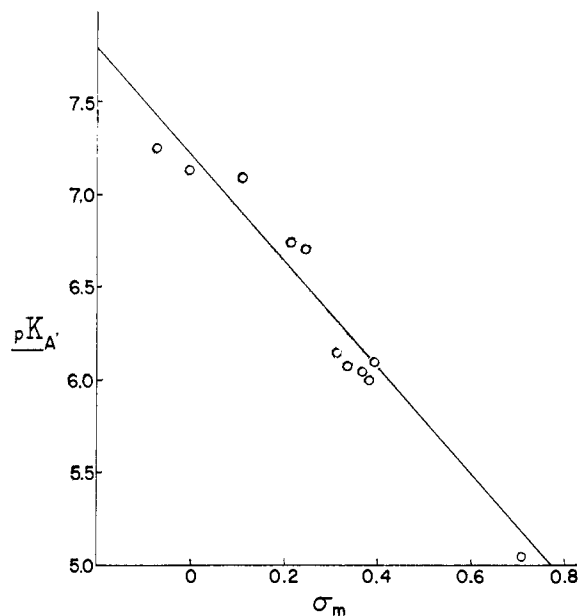
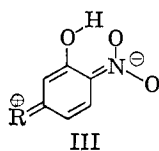


Fig. 1.—The relationship between pK_A and σ_m for 5-substituted 2-nitrophenols.

expected across the ring, and the normal electronic properties associated with both groups would be modified. The 5-substituent would show a greater electron-donating influence than Hammett's σ_m value would indicate. At the same time, the nitro group, which experiences an increased electron density at its point of attachment to the ring, will suffer a reduction in its deactivating influence, relative to the case where the 5-substituent is not of an electron-releasing type. Structure III is a representation of the type of resonance interaction here discussed.

Any modification of the electronic properties of the nitro group or the 5-substituent would be expected to affect the ionization constants of the phenols. The



over-all effect may best be considered as a summation of three individual effects. First, the 5-substituent is displaying a greater tendency to release electrons than normal. Thus, the electron density on the ring is greater, and so the phenolic group less readily releases a proton. Second, and operating in the same direction as the first effect, is the reduction in the deactivating influence of the nitro group. The third effect is the change in strength of the intramolecular hydrogen bond, but in this case it is difficult to predict the direction of the effect, since two opposing influences make contributions. The oxygen atoms in the nitro group become more basic, thereby strengthening the hydrogen bond, while the decreased acidity of the phenolic hydrogen will weaken the hydrogen bond.

However, the first two effects tend to lower the ionization constants of the phenols. In order to make allowance for this lowering, it would seem desirable to introduce into the Hammett treatment some quantity which measures the ability of a substituent to donate electrons by resonance to an extent greater than normally displayed in the ionization of benzoic acids.

In an attempt to obtain a more quantitative relationship for these qualitative suggestions, multiple regression analyses^{8b} were carried out using σ_p^+ ,⁹ σ_p^- ,^{4a,d} σ_p ,⁴ⁿ and cross-products of each of these independently with σ_m . No significance could be attached to any of the cross-products. In only one case could it be said that a significant contribution was made by the introduction of an additional variable. This variable was the σ_p^+ value, which, for electron-withdrawing substituents, is numerically similar to σ_p values, but for strongly electron-donating groups it is considerably more negative. Equation 3 was obtained, where R is the multiple correlation coefficient.

$$\begin{aligned} \text{p}K_A &= 7.09 - 2.53\sigma_m - 0.307\sigma_p^+, \\ &\quad (0.001) \quad (0.031) \\ R &= 0.986, s = 0.123 \quad (3) \end{aligned}$$

The numbers in parentheses below the two coefficients of eq. 3 are probability levels as measured by "Student's" t -tests.^{8c} From these values, it can be seen that a small, but significant, contribution is made by the p -effect. The negative coefficient of σ_p^+ in eq. 3 shows that the $\text{p}K_A$ increases as the 5-substituent becomes more strongly electron releasing. Probably, this increase in the $\text{p}K_A$ results from an increase in the strength of the intramolecular hydrogen bond and an accompanying decrease in ease of dissociation of the proton.

There are two observations which may be made about this relationship. First, the value for $\text{p}K_A^\circ$ is decreased to 7.09, which more closely approximates the experimentally measured value of 7.13 than that obtained in the linear regression (7.22). Second, the value for ρ_m increases to -2.53 , which more closely approaches the value of -2.11 ^{4c} anticipated according to Jaffé's assumption.^{4b}

The possibility of a relationship existing between the wave number difference, $\Delta\nu = \nu_B - \nu_A$, and Hammett's σ -values or $\text{p}K_A$ was investigated statistically. No direct relationship was found. The inclusion in the regression analysis of the variables already discussed (σ_p^+ , σ_p^- , σ_p , and cross-products of each with σ_m) gave no significant improvement.

A poor correlation was obtained between ν_A and ν_B , the acidic and alkaline wave numbers of the 5-substituted 2-nitrophenols. However, examination of the deviation from regression of each of the substituents showed that the deviation for the phenyl substituent was almost twice the standard deviation. The regression was carried out omitting the value for the phenyl substituent, and eq. 4, plotted in Fig. 2, was obtained.

$$\nu_B = -5479 + 1.03\nu_A, r = 0.928, s = 270 \quad (4)$$

Equation 4 is analogous to the corresponding equation found previously for 4-substituted 2-nitrophenols⁸ and again indicates that the substituents perform similar roles in both acid and alkaline series. However, in contrast to the results found for 4-substituted 2-nitrophenols, no good relationship was found between σ_m and ν_A , or between σ_m and ν_B . Even ignoring the results for the phenyl substituent, the equations had very low correlation coefficients of -0.150 and -0.511 . One fact is consistent, nevertheless, and it concerns all substituents capable of electron release, whether the mechanism be inductive or resonance (this includes halogen substituents). These substituents all produce a shift of the absorption maximum in both acidic and alkaline solution toward shorter wave length relative to that of unsubstituted 2-nitrophenol. Conversely, all substituents capable of electron-withdrawal through resonance produce a shift to longer wave length relative to that of unsubstituted 2-nitrophenol. These shifts are in the reverse direction to those observed for 4-substituted 2-nitrophenols.⁸ It was found that the difference, $\Delta\nu_A^*$, *i.e.*, the wave number for a 5-substituted 2-nitrophenol minus the wave number for the 4-substituted 2-nitrophenol with the *same* substituent, was related to the difference $(\sigma_p^\pm - \sigma_m)$, where σ_p^\pm is the σ_p^+ or the σ_p^- value, whichever is applicable. A similar type of relationship was found for $\Delta\nu_B^*$ for the corresponding 4- and 5-substituted 2-nitrophenoxide ions, and these results are illustrated in Fig. 3 and 4. Linear regression analyses of $\Delta\nu^*$ on $(\sigma_p^\pm - \sigma_m)$ values shown in Table II for the phenol and phenoxide species give eq. 5 and 6. The values for the phenyl substituent

$$\begin{aligned} \Delta\nu_A^* &= -29.66 - 3569(\sigma_p^- - \sigma_m), \\ r &= -0.967, s = 495 \quad (5) \end{aligned}$$

$$\begin{aligned} \Delta\nu_B^* &= -415.7 - 2996(\sigma_p^\pm - \sigma_m), \\ r &= -0.959, s = 425 \quad (6) \end{aligned}$$

were omitted from the calculations leading to eq. 5. The difference $(\sigma_p^\pm - \sigma_m)$ at first glance appears to be a somewhat meaningless quantity, but, in fact, it is an approximate measure of the maximum resonance contribution any substituent may make in either the 4- or 5-substituted 2-nitrophenols. Equations 5 and 6 show that as the resonance electron-donating properties of the substituent increase [*i.e.*, $(\sigma_p^\pm - \sigma_m)$ becomes more negative], the differences in wave numbers

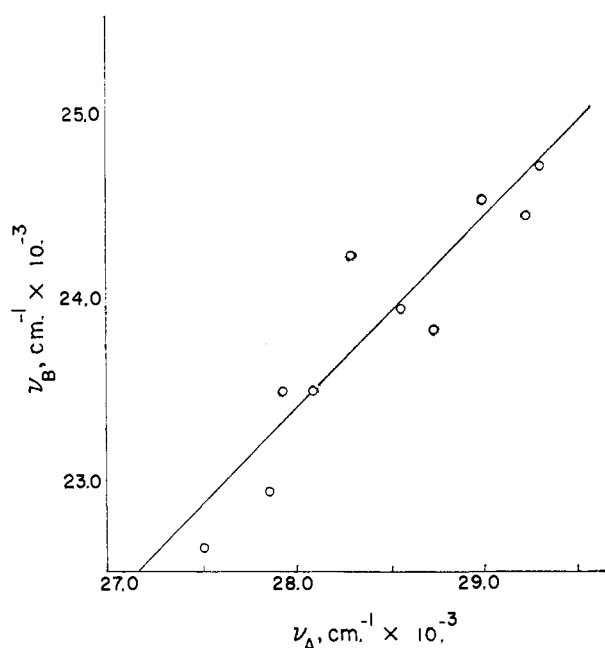


Fig. 2.—The relationship between ν_B and ν_A for 5-substituted 2-nitrophenols.

($\Delta\nu_A^*$ and $\Delta\nu_B^*$) become increasingly positive. On the other hand, as the resonance electron-withdrawing properties increase [i.e., $(\sigma_p^\pm - \sigma_m)$ becomes more positive], the differences between the wave numbers become increasingly negative. The data in Table II show that the excitation energy of a substituted 2-nitrophenol relative to that of unsubstituted 2-nitrophenol is lowered when either two resonance electron-withdrawing groups are *para* to each other in a 5-substituted 2-nitrophenol, or two resonance electron-donating groups are *para* to each other in a 4-substituted 2-nitrophenol. On the other hand, in either of the two series, when the variable substituent is in a position *para* to a group which has an opposite resonance electronic effect, the excitation energy is raised. Before attempting to rationalize this observation in terms of resonance effects, the significance of the extinction coefficients will be considered.

TABLE II
DIFFERENCE IN WAVE NUMBER BETWEEN 4- AND
5-SUBSTITUTED 2-NITROPHENOLS

Subst.	$\Delta\nu_A^*{}^a$	$\Delta\nu_B^*{}^b$	$(\sigma_p^\pm - \sigma_m)^c$
CH ₃ O	3410	2530	-0.893
CH ₃	1560	720	- .380
CH ₂ CONH	1660	900	- .717
H	0	-230	0
C ₆ H ₅	4130 ^d	970	-0.397
Cl	1620	950	- .259
CO ₂ CH ₃	-1240	-1530	.321
CO ₂ C ₂ H ₅	-1390	-1590	.308
COOH	1410373
COO ⁻	...	-1160	.247

^a $\Delta\nu_A^*$ (cm.⁻¹) = ν_A (5-position) - ν_A (4-position). ^b $\Delta\nu_B^*$ (cm.⁻¹) = ν_B (5-position) - ν_B (4-position). ^c $(\sigma_p^\pm - \sigma_m)$ = $(\sigma_p^+, \text{ref. 9, or } \sigma_p^-, \text{ref. 4a, whichever is applicable}) - \sigma_m$, ref. 4a. ^d This value is so high that its introduction into the regression analysis considerably reduces the significance level.

It may be said that, for a closely related series of compounds, the extinction coefficient is roughly proportional to the integrated intensity,¹⁰ which is dif-

(10) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 249.

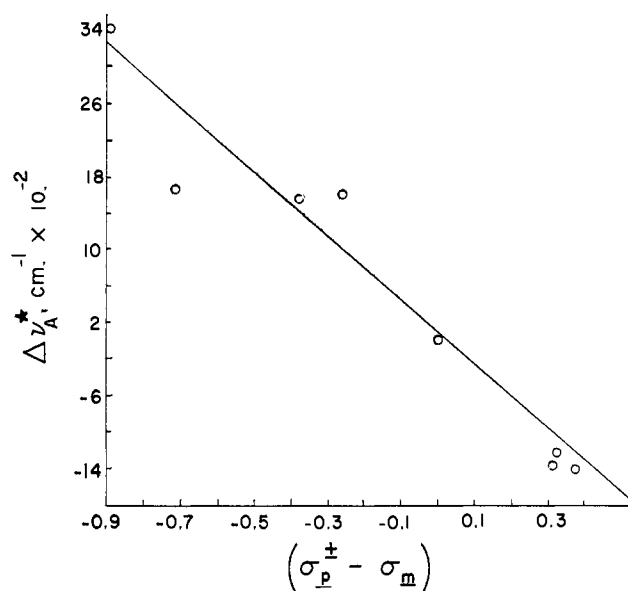


Fig. 3.—The relationship between $(\sigma_p^\pm - \sigma_m)$ and $\Delta\nu_A^*$, the wave number for a 5-substituted 2-nitrophenol minus the wave number for the corresponding 4-substituted 2-nitrophenol.

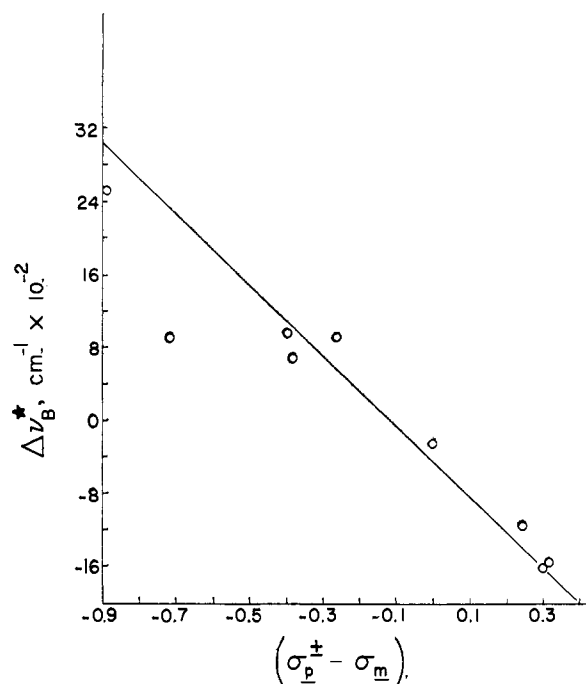


Fig. 4.—The relationship between $(\sigma_p^\pm - \sigma_m)$ and $\Delta\nu_B^*$, the wave number for a 5-substituted 2-nitrophenoxide ion minus the wave number for the corresponding 4-substituted 2-nitrophenoxide ion.

ficult to measure when the absorption peaks are not separated. The integrated intensity acts as a measure of the transition probability and, to some extent, of the polarization of the molecule.¹¹ Therefore, the extinction coefficient also acts as an approximate measure of these quantities. The extinction coefficients for 4-substituted 2-nitrophenols were all found to have the same order of magnitude which is evidence in favor of the suggestion that identical transitions are taking place throughout the series. In the 5-substituted 2-nitrophenols, the extinction coefficients were also found to

(11) E. A. Braude, "The Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Eds., Academic Press, Inc., New York, N. Y., 1955, p. 135.

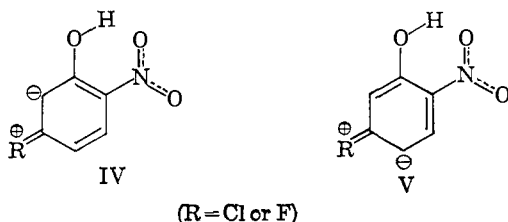
have a constant order of magnitude, except for the 5-methoxy-, 5-phenyl-, and 5-acetamido-2-nitrophenols. For each of these three compounds the extinction coefficient was found to be higher than the value for the corresponding phenoxide ions. However, on running the spectra of the 5-substituted 2-nitrophenols in cyclohexane, the extinction coefficients became more nearly equal (*ca.* 4.5×10^3) as shown in Table III. The most useful conclusion which may be drawn from this observation is that the electronic states of the molecules involving the substituents methoxy, acetamido, and probably phenyl are in some way solvent dependent. A complete appreciation of the actual states involved is not possible using only the data on the extinction coefficient. Nevertheless, it may be tentatively suggested that the high extinction coefficient in aqueous solution is attributed to a strong contribution from the polar structure III. Such a structure would be highly stabilized by a polar solvent, but not significantly stabilized by a nonpolar solvent.

TABLE III
ULTRAVIOLET SPECTRAL RESULTS FOR 5-SUBSTITUTED
2-NITROPHENOLS IN CYCLOHEXANE SOLUTION

5-Subst.	$\lambda_{C_6H_{12}}^a$	$\Delta\lambda^b$	$\Delta\lambda_{C_6H_{12}}^c$	$\Delta\lambda_{H_2O}^d$	$\epsilon_{C_6H_{12}}^e \times 10^{-3}$	$\epsilon_{H_2O}^e \times 10^{-3}$
CH ₃ O	340.0	5.0	5.5	5.0	4.5	11.1
CH ₃	348.0	0.0	-2.5	2.0	4.6	4.2
H	345.5	4.5	0.0	0.0	3.6	3.3
CH ₃ CONH	342.0	11.0	2.5	-3.0	1.1	11.2
CO ₂ C ₂ H ₅	356.0	2.0	-10.5	-8.0	4.4	3.6
Cl	341.5	0.5	4.0	8.0	5.3	4.5
F	337.5	3.5	8.0	9.0	3.9	3.8
NO ₂	353.5	9.5	-8.0	-13.0	2.2	3.8
CHO	362.0	-3.0	-16.5	-9.0	4.3	3.5
C ₆ H ₅	313.0	15.0	32.5	22.0	...	14.2
COOH	343.0	13.0	2.5	-6.0	...	3.4

^a $\lambda_{C_6H_{12}} (m\mu) = \lambda_{max}^{C_6H_{12}}$. ^b $\Delta\lambda (m\mu) = \lambda_{max}^{HCl} - \lambda_{max}^{C_6H_{12}}$. ^c $\Delta\lambda_{C_6H_{12}} = \lambda_{max}^{HCl} (for R = H) - \lambda_{max}^{C_6H_{12}} (for R)$. ^d $\Delta\lambda_{H_2O} = \lambda_{max}^{HCl} (for R = H) - \lambda_{max}^{HCl} (for R)$. ^e $\epsilon_{C_6H_{12}} =$ extinction coefficient in C₆H₁₂. ^f Solubility too low for accurate measurement of $\epsilon_{C_6H_{12}}$.

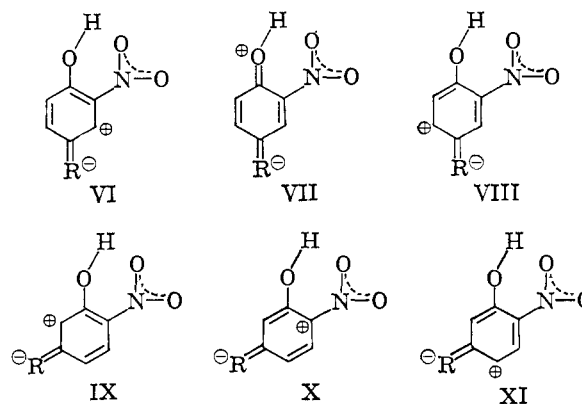
The wave number shifts observed for the chloro and fluoro substituents in the two solvents suggest that a solvent effect operates here also. Structures III to V probably contribute more to the excited state than to the ground state. The resonance structures



involving the phenolic and 2-nitro groups alone are omitted, since they are common throughout the series. In the ground state the electrons are displaced toward the substituent through an electron-attracting inductive effect, while in the excited state the substituent experiences a migration of electrons toward the ring through the resonance electron-donating property. Thus, the orientation of the highly polar solvent molecules is unfavorable for stabilization of the excited state in view of the Franck-Condon principle that the distance moved by the nuclei during an electronic ex-

citation is negligible. Therefore, the water molecules, which have the necessary orientation for stabilization of the ground state, have insufficient time to reorient themselves to stabilize the oppositely polarized excited state. Consequently, the energy of the excited state is raised which in turn causes the absorption peak to move to shorter wave length. In the nonpolar solvent, no significant solvation of either state can occur. Therefore, the excitation energy should be lowered. Taking into account the wave length shift for unsubstituted 2-nitrophenol in the two solvents, it can be seen that the excitation energies for the 5-chloro- and 5-fluoro-2-nitrophenols are in fact reduced.

In the case of resonance electron-attracting substituents in the 4- and 5-substituted 2-nitrophenols, one may construct the resonance structures VI to XI.

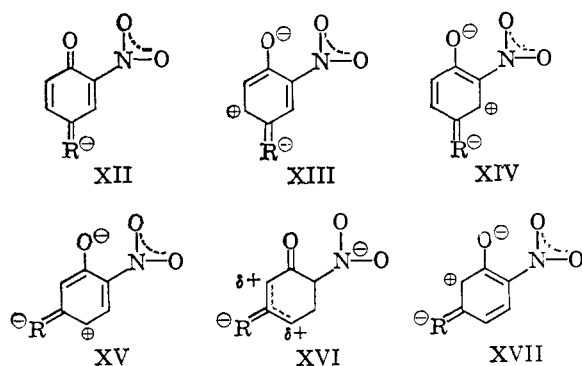


Again, one might anticipate that solvent effects would make some contribution to the stability of one state relative to the other. However, the evidence from the spectra in nonpolar cyclohexane is inconclusive. For example, in the 5-substituted series, one would expect that structures of the type IX to XI would contribute more to the excited state than to the ground state and thus stabilize the excited state more than the ground state. Whereas this influence and the solvent effect work in opposite directions in the case of resonance electron donors, in this case they should augment each other. This is attributed to the fact that the substituents have only electron-withdrawing properties, and, consequently, the slight polarization in the ground state becomes considerably enhanced in the excited state. Since a polar solvent can provide greater stabilization for a more polar group, the excited state should be stabilized more than the ground state. The combination of these two stabilizing influence would be expected to create a shift to longer wave length.

On changing to a nonpolar solvent, the excited states of these molecules would lose their solvent stabilization, therefore the excitation energy would become greater. Such an effect is observed for the 5-nitro- and 5-carboxy-substituted 2-nitrophenols, but not for the 5-aldehyde or the 5-carbomethoxy compound. It is best under these circumstances to neglect any possible solvation effect, as it is likely to be too complex to help explain the difference between the absorption spectra of the 4- and 5-substituted 2-nitrophenols. Also, in the absence of data in nonpolar solvents for the 4-substituted 2-nitrophenols, any explanation regarding the observed hypsochromic shift would be

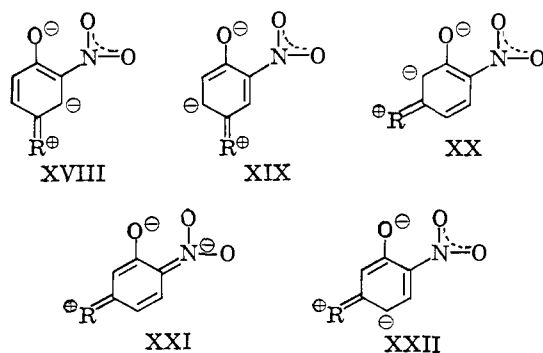
open to question. However, one can say that a structure of type VII could conceivably be sufficiently stable that it makes a significant contribution to the ground state. The observation that the greater the electron-withdrawing ability of the substituent the larger the hypsochromic shift supports this suggestion. This is the case because structure VII becomes more probable as the electron-withdrawing character of the substituent increases.

Turning to the series of nitrophenoxide ions, the over-all pattern remains similar. Again, the wave number shift of a substituent in the 5-position is in the reverse direction to that observed for the same substituent in the 4-position. However, in both series, the extinction coefficient remains essentially constant, which is evidence in support of the suggestion that in each series an identical transition is being observed. For the indicated series of resonance electron-withdrawing substituents, structures XII to XVII may be said to be resonance contributors to the two series.



Despite the lack of more substantial data, one may say that structures of the type XII could make significant contributions to the ground state, and one would expect them to be solvent stabilized, thereby raising the excitation energy for the 4-substituted 2-nitrophenols. No such stable structure may make a contribution to the 5-substituted 2-nitrophenols, since, in this case, the electron-withdrawing groups are *para* to one another. Therefore, one would anticipate that the structures represented by XV to XVII make a greater contribution to the excited state than to the ground state, thereby lowering the excitation energy.

The structures for resonance electron-releasing substituents may be represented by XVIII to XXII.



With reservations, one might suggest that the ground state is preferentially stabilized when direct resonance across the ring is possible, as in structure XXI, thus raising the excitation energy for the 5-substituted 2-

nitrophenols. On the other hand, structures of the type XVIII and XIX contribute mainly to the excited state, thereby lowering the excitation energy for the 4-substituted 2-nitrophenols.

There is an interesting difference to be observed in the degree of shift for the two series. The bathochromic shift in the 4-substituted 2-nitrophenols is considerably larger than the hypsochromic shift in the 5-substituted 2-nitrophenols. Also, the greater the resonance electron-donating capacity of any substituent, the greater is the separation between the two absorption maxima. This is useful evidence in support of the suggestion that the resonance capabilities of the substituent tend to stabilize different states in the 4- and 5-substituted 2-nitrophenoxides. As mentioned previously in connection with the regression analysis of σ_m on pK_A , the value of ρ (the reaction constant) obtained was larger than anticipated. This too was attributed to additional resonance between the resonance electron-releasing substituent in the 5-position and the 2-nitro group.

Experimental

2,5-Dinitrophenol, 2-nitrophenol, and 3-hydroxy-4-nitrobenzoic acid were obtained from commercial sources. Eight of the 5-substituted 2-nitrophenols were prepared by methods previously reported in the literature, as indicated by footnotes to Table IV. 5-Acetamido-2-nitrophenol was prepared by slowly adding, at -10° over a period of 1 hr., a slight excess of fuming nitric acid (d 1.5) in two volumes of glacial acetic acid to a solution of 3-acetamidophenol in an equal volume of glacial acetic acid. The mixture was stirred at -5 to -10° for 1 hr., poured onto three volumes of ice, and filtered. The precipitate was extracted with 5% sodium hydroxide solution and the extract was evaporated until crystallization occurred upon cooling. The resulting crystals were mainly 3-acetamidophenol. The filtrate was evaporated further and a second crop of crystals appeared. These were separated and refluxed for 2 hr. with an excess of dilute hydrochloric acid. Careful neutralization with ammonium hydroxide produced yellow crystals of 5-amino-2-nitrophenol (m.p. $158-160^\circ$). This amine was warmed with acetic anhydride, the product was poured onto an ice-water mixture, and the precipitate was recrystallized from 75% aqueous ethanol to ob-

TABLE IV
MELTING POINTS OF 5-SUBSTITUTED 2-NITROPHENOLS

5-Subst.	M.p., $^\circ\text{C.}$ (cor.)	Lit. m.p., $^\circ\text{C.}$
H	45-46	45 ^{a,b}
NO ₂	107-108	108 ^{a,c}
CH ₃	55-56	56 ^d
Cl	39-40	41 ^e
COOH	229-230	230 ^{a,f}
CO ₂ CH ₃	90.5-91	92 ^{f,g}
CO ₂ C ₂ H ₅	84-85	84 ^{f,g}
CH ₃ O	91.5-92.5	91.5 ^h
C ₆ H ₅	101-101.5	103 ⁱ
F	29-30	32 ^j
CH ₃ CONH	217-218	221 ^k (200) ^l
CHO	129-130	128 ^m

^a Obtained commercially. ^b I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1953, p. 756. ^c Footnote b, Vol. II, p. 386. ^d G. P. Gibson, *J. Chem. Soc.*, 123, 1269 (1923). ^e H. H. Hodgson and F. H. Moore, *ibid.*, 127, 1600 (1925). ^f Footnote b, Vol. III, p. 700. ^g Prepared by simple esterification of 4-nitro-3-hydroxybenzoic acid. ^h J. Kinugawa, M. Ochiai, and H. Yamamoto, *Yakugaku Zasshi*, 79, 931 (1959); *Chem. Abstr.*, 54, 497f (1960). ⁱ J. C. Colbert, W. Meigs, and R. L. Jenkins, *J. Am. Chem. Soc.*, 59, 1122 (1937). ^j As in footnote e, using 3-fluorophenol. ^k R. Meldola and F. G. C. Stevens, *J. Chem. Soc.*, 89, 925 (1906). ^l G. A. Barbaglia, *Chem. Ber.*, 7, 1259 (1874). ^m P. Friedlaender and O. Schenck, *ibid.*, 47, 3040 (1914).

tain yellow crystals of 5-acetamido-2-nitrophenol (m.p. 217–218°). The observed melting points of the 5-substituted 2-nitrophenols are shown in Table IV.

The absorption spectra and pK_A 's of 1×10^{-4} M solutions of the 5-substituted 2-nitrophenols were measured as described previously.⁶ However, for the least soluble compounds, these measurements were made on 1×10^{-5} M solutions in 10-cm. cells. The results are shown in Table I.

By the same procedure, the absorption spectra of 1×10^{-4} M cyclohexane solutions of the 5-substituted 2-nitrophenols were obtained. For 5-phenyl- and 5-carboxy-2-nitrophenols, owing to very low solubilities, the final concentrations were unknown and extinction coefficients were not calculated. For these two

very slightly soluble compounds, 10-cm. spectrophotometer cells were used. The spectral data for the cyclohexane solutions are given in Table III.

Acknowledgments.—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.

[CONTRIBUTION NO. 989 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON, DEL.]

Hydrogen Bonding in Fluoro Alcohols

By W. J. MIDDLETON AND R. V. LINDSEY, JR.

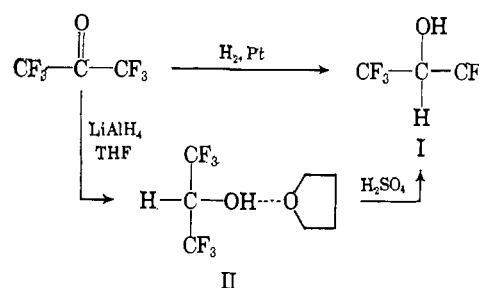
RECEIVED JULY 6, 1964

A number of new secondary and tertiary fluoro alcohols and diols have been synthesized. These alcohols are extremely strong hydrogen-bonding donors, as is evidenced by their solvent properties, complex formation, acidities, and infrared and nuclear magnetic resonance spectra.

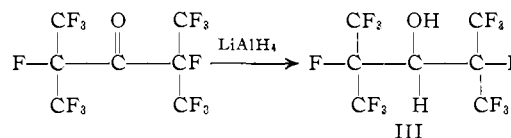
Aliphatic alcohols that contain a high percentage of fluorine are more acidic than the corresponding fluorine-free alcohols¹ and thus would be expected to be stronger hydrogen-bonding acids.² The most pronounced effects would be observed in alcohols containing fluorine bonded directly to the α -carbon. One such alcohol, perfluorocyclobutanol, has been prepared, and n.m.r. studies indicate that it is internally hydrogen bonded.³ However, this alcohol is thermally unstable. Alcohols that contain two or three perfluoroalkyl groups attached to the α -carbon would also be expected to be strong hydrogen-bonding acids. We have synthesized a number of these more stable secondary and tertiary fluoro alcohols and diols and have found that their most dominate characteristic is their ability to function as extremely strong hydrogen-bonding donors.

Synthesis.—A number of secondary fluoro alcohols were prepared by reduction of the corresponding fluoro ketones. Both catalytic and chemical reduction of hexafluoroacetone have given 2H-hexafluoro-2-propanol⁴ (I) in high yield. The product prepared by reduction of hexafluoroacetone with lithium aluminum hydride in tetrahydrofuran (THF) followed by the usual acid work-up was the 1:1 tetrahydrofuran complex of the alcohol II. This complex is stable at its atmospheric boiling point, and is water immiscible (both I and tetrahydrofuran are miscible with water). The alcohol was freed from this complex with fuming sulfuric acid.

Other fluoro ketones, including 1,3-dichlorotetrafluoroacetone, 1,1,3-trichlorotrifluoroacetone, 1,1,3,3-tetrachlorodifluoroacetone, and bis(perfluoroisopropyl)ketone, also were reduced with lithium aluminum hy-

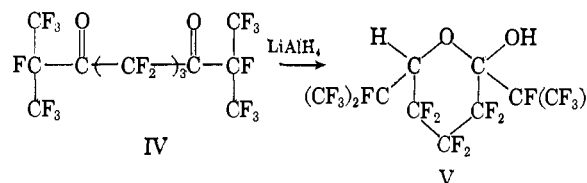


dride in tetrahydrofuran to form the corresponding complexes from which the free alcohols were obtained by treatment with sulfuric acid. The F^{19} n.m.r. spec-



trum of bis(perfluoroisopropyl)carbinol (III) is of particular interest, for it shows two different types of CF_3 groups, although there is no formally unsymmetrical carbon atom and no significant amount of restricted rotation. This nonequivalence arises because the geminal CF_3 groups are bonded to a carbon which in turn is bonded to a carbon bearing three different groups, allowing the CF_3 groups to be in different magnetic environments.

An attempt to prepare a diol by reduction of the perfluorodiketone IV with lithium aluminum hydride gave instead the cyclic ether V.



Catalytic hydrogenation of hexafluoroacetone with platinum oxide at 150° gave I in 90% yield. Several

(1) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958.

(2) G. C. Pimental and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(3) S. Andreades and D. C. England, *J. Am. Chem. Soc.*, **83**, 4670 (1961).

(4) I. L. Knunyants, Russian Patent 138,604 (1961), has reported the preparation of this alcohol by reduction of hexafluoroacetone with sodium borohydride, and a recent Belgian Patent, 634,368 (1963), reports the preparation by catalytic reduction of hexafluoroacetone with hydrogen at 200–450° in the presence of Cu-CrO₃ catalyst.