acetate gave pure VIII: mp 298–299°; λ_{max}^{KBr} 2.83, 3.05, 3.10, 3.19 (NH), 5.80, 5.95 (C═N), 6.14, and 6.51 μ (NH bending); λ_{max}^{EtOH} 212 mμ (ε 2820).

Anal. Calcd for $C_5H_4Cl_4F_8N_4O$: C, 21.2; H, 1.4; Cl, 25.1; F, 26.8; mol wt, 283. Found: C, 21.6; H, 1.7; Cl, 25.0; F, 26.3; mol wt (cryoscopic in dimethyl sulfoxide), 267.

2,2,4,4-Tetrakis(trifluoromethyl)-6-amino-4H-1,3,5-dioxazine (IIb).—A solution of 4.95 g (0.12 mole) of cyanamide in 30 ml of ether was added to 80 g (0.48 mole) of hexafluoroacetone in 125 ml of ether over a 10-min period. The temperature rose from −15 to −2° and was held at −2° for 1.5 hr. The volatile solvent and excess hexafluoroacetone were then removed under vacuum at room temperature and an oil resulted. The oil was taken up in methylene chloride and extracted with water and the organic solution was dried and evaporated to give 32.3 g (72%) of crude IIb. The product was crystallized from pentane to give pure IIb: mp 67–69°; λ_{max}^{KBr} 2.87, 3.05, 3.10, 3.16 (NH), and 5.80 μ (C═N).

Anal. Calcd for $C_7H_2F_{12}N_2O_2$: C, 22.4; H, 0.5; F, 60.4; N, 7.5. Found: C, 22.8, 22.7; H, 0.9, 0.7; F, 60.7, 60.8; N, 7.9, 8.0.

Decomposition of IIb.—A solution of 6.65 g (0.0178 mole) of IIb in 50 ml of xylene was heated for 1 hr at 110–130°. A total of 2.0 g of hexafluoroacetone was collected in a cold trap after passing through a 0° condenser. On cooling, 3.0 g of crystalline material separated and was collected, which on the basis of proton nmr was shown to consist of 2.08 g of VI and 0.92 g of VII.

Sublimation of the mixture (1.0 g) at 90° (1 mm) gave 0.60 g of pure tetrahydro-2,2,6,6 tetrakis(trifluoromethyl)-4H-1,3,5-oxadiazin-4-one (VI), mp 175–177°, isomeric with IIb; λ_{max}^{Nujol} 3.1, 3.22 (NH), 5.84 (C═O), and 6.70 μ (NH bend).

Anal. Found: C, 21.6, 21.6; H, 0.6, 0.7; F, 59.5; N, 7.6, 7.7.

Continued sublimation at 90–130° causes some VII to sublime, however, it deposits in a second layer closer to the heat source. Sublimation was continued at 130° until no further VI was observed and the temperature was raised to 170° whereupon the bulk of VII sublimed and was collected (0.20 g): mp 222–226°; λ_{max}^{Nujol} 3.1, 3.25 (NH), 5.78, 5.90 (C═O), and 6.60 μ (NH bend).

Anal. Calcd for $C_5H_3F_6N_3O_2$: C, 23.9; H, 1.6; F, 45.4; N, 16.7. Found: C, 23.7; H, 1.2; F, 45.7; N, 16.7.

In a second experiment the volatiles collected after decomposition under vacuum were shown by mass spectrometry to be ~85% hexafluoroacetone and ~15% hexafluoroacetone imine.

Preparation of VIII from Ib.—A solution of 10 g of Ib in 500 ml of 1,2,4-trichlorobenzene was heated for 15 min at 215°. The solution was quickly filtered and after cooling 7.0 g of VIII (70%) was isolated by filtration.

Pyrolysis of (1:1) Ketone–Cyanamide Adduct.—The oil IVb (14g) formed by contacting cyanamide and dichlorotetrafluoroacetone at 0–10°, followed by evaporation of the solvents, was heated at 100° for a few minutes. Dichlorotetrafluoroacetone (3g, 52%) was recovered along with 4.4 g (54%) of Ib.

Preparation of Acetyl Ib.—Approximately 24 g (0.1 mole) of the above oil IVb was heated at 52° for 16 hr with 10.2 g (0.10 mole) of acetic anhydride. Filtration gave 2.2 g (7%) of acetyl compound which melted at 222–222.5° after recrystallization from acetone–ether: λ_{max}^{KBr} 2.95, 3.04, 3.09, 3.14 (NH), 5.64, 5.88 (C═N), 6.04 (C═O), and 6.53 μ (–NH bend).

Anal. Calcd for $C_7H_6Cl_2F_4N_4O_2$: C, 25.9; H, 1.9; Cl, 21.9; F, 23.4; N, 17.2. Found: C, 26.0; H, 2.0; Cl, 21.5; F, 23.1; N, 17.0.

Attempted Preparation of Acetyl Derivative from Ib. Formation of IX.—A solution of 6 g (0.021 mole) of Ib was refluxed for 2 hr in 100 ml of acetic anhydride. The solution was evaporated to 20 ml, and ether was added along with decoloring charcoal. After allowing this mixture to stand for 1 hr, the ether was evaporated, methanol was added, and the whole solution was filtered into water to give 3.3 g (45%) of IX. After crystallization, IX has mp 230–231°; λ_{max}^{KBr} 3.05, 3.10, 3.20 (NH), 5.77, 5.86 (C═N), 5.95 (C═O), and 6.65 μ (NH bend); λ_{max}^{EtOH} 235 mμ (ε 5040).

Anal. Calcd for $C_7H_6Cl_2F_4N_4O_2$: C, 25.9; H, 1.9; Cl, 21.9 F, 23.4. Found: C, 25.7; H, 2.2; Cl, 21.5; F, 22.7.

Preparation of Dichlorotetrafluoroacetone–Dicyandiamide (2:1) Adduct.—Dicyandiamide (8.4 g, 0.10 mole) was heated to 50° in 100 ml of acetonitrile. To this slurry was added 25 ml of dichlorotetrafluoroacetone so that the temperature rose to 80° and the solid completely dissolved. On cooling to 0°, 34.8 g of product was obtained: mp 274.5–275°. From the solvent another 2.0 g was obtained totaling 36.8 g (78%): λ_{max}^{KBr} 2.85, 3.05, 3.10, 3.26 (NH), 5.83, 5.90, 5.96 (C═O or C═N), 6.22, and 6.46 μ; λ_{max}^{EtOH} 214 mμ (ε 14,650).

Anal. Calcd for $C_8H_4Cl_4F_8N_4O_2$: C, 19.9; H, 0.8; Cl. 29.4; F, 31.5; N, 11.6; mol wt, 482. Found: C, 20.4; H, 1.0; Cl, 29.4; F, 31.6; N, 11.5; mol wt (cyroscopic in dimethyl sulfoxide), 449.

Derivatives of 1-Phenylazo-2-Naphthylamine. The Effect of Substituent on Color

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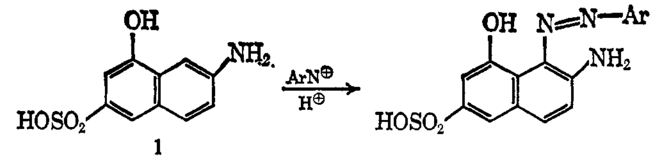
7-Amino-1-naphthyl acetate couples with diazonium salts at pH 4–5 only in the 8 position to give, after hydrolysis, pure 1-arylazo-2-amino-8-naphthols. An earlier observation that the color of these dyes is insensitive to acids and alkali, an effect presumably caused by strong hydrogen bonding with the azo group, has been confirmed. The visible absorption band centroids of these dyes are found to lie at 58 ± 2 mμ longer wavelengths than those of the corresponding 1-arylazo-2-naphthylamines and their values, for both dye systems bearing *meta* and *para* substituents on the phenylazo group, show good correlation with the Hammett and Taft σ values. The influence of substituents on color is examined.

Arylazo derivatives prepared from "γ acid" [7-amino-1-naphthol-3-sulfonic acid (1)] by coupling at the 8 position with diazonium salts in acid solution are well-established red to purple water-soluble dyes used commercially for color-fast dyeing of cotton.[3]



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In 1951, Perekalin and Slabachevskaya[4] described the preparation of the parent azo dye free of the sulfonic acid group, 1-phenylazo-2-amino-8-naphthol (2),

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[1] To whom inquiries should be directed: RCA Laboratories, Princeton, N. J.

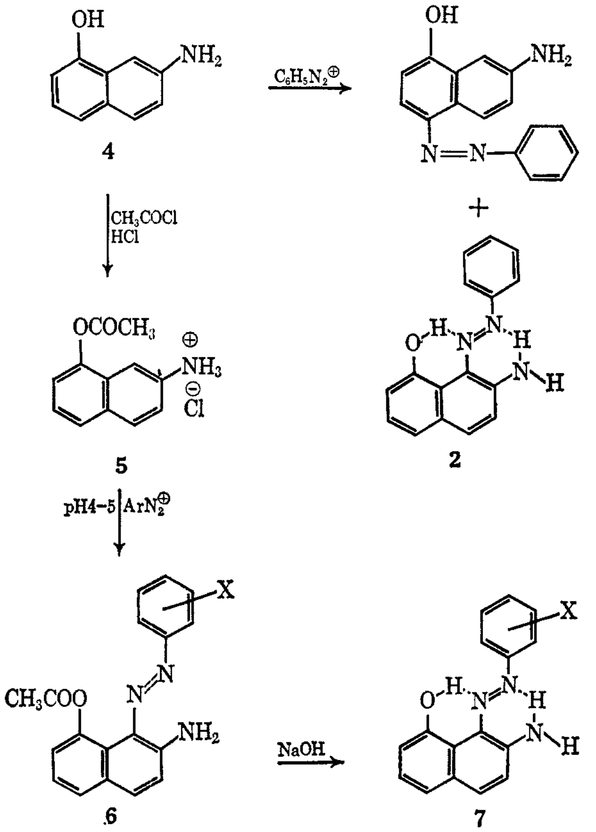
[2] Thayer Academy Advanced Studies in Science, summer 1961.

[3] See, for example, Colour Index No. 17020 ff, "Colour Index," 2nd ed, The Society of Dyers and Colourists, England, 1956; H. E. Woodward in "The Chemistry of Synthetic Dyes and Pigments," H. A. Lubs, Ed., Reinhold Publishing Corp., New York, N. Y., 1955, p 123 ff.

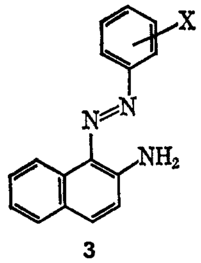
[4] V. V. Perekalin and N. M. Slabachevskaya, *J. Gen. Chem. USSR*, **21**, 985 (1951).

and reported that its visible absorption spectrum was unchanged in either acidic or basic solution. They suggested that both the 2-amino group and the 8-hydroxy group were involved in six-membered rings containing strong hydrogen bonds to the azo group (see 2 in Chart I) and that, for this reason, both groups had lost their usual respective basic and acidic properties.

Chart I



We have had occasion to prepare a number of derivatives of 2 bearing substituents on the benzene ring and thought that a systematic study of the influence of substituent on the visible absorption spectra of this system might permit some conclusions to be drawn regarding the properties of the electronic transition involved and the role that hydrogen bonding plays in the excited state. As a basis for comparison, a similar series of 1-arylazo-2-naphthylamines (3) was prepared.



3

Preparation of Dyes.—Perekalin and Slabachevskaya[4] prepared 2 by the reaction of a benzenediazonium salt with 7-amino-1-naphthol (4) in acid solution followed by chemical separation of the mixture of dyes obtained as a result of coupling at both the 4 and 8 positions (Chart I). They studied the influence of the pH of the coupling medium on the rate and products of the reaction, and found that, as the pH was lowered, the formation of the undesired dyes was suppressed, but also that the rate of the reaction decreased. We anticipated that, especially with the slower reacting diazonium salts bearing electron-donating substituents, this decrease in rate might allow the slow, acid-catalyzed decomposition of the diazonium salt to become a major competing reaction and thus even further complicate the isolation and purification of the desired products.

In order to suppress coupling into the hydroxy-substituted ring as completely as possible and simultaneously to permit the coupling to be carried out at a pH (4–5) which would give a maximum rate, the hydroxyl group of 7-amino-1-naphthol was "masked" by esterification.[5] In aqueous acetic acid buffered at pH 4–5, 7-amino-1-naphthyl acetate hydrochloride (5) coupled readily with all of the diazonium salts used in this work to give the corresponding 1-arylazo-8-acetoxy-2-naphthylamines (6). These yellow-orange dyes were usually isolated from the coupling reaction as low-melting solids or gums, which, without prior purification, were converted to pure 1-arylazo-2-amino-8-naphthols (7), by mild basic hydrolysis. During the hydrolysis reactions, the color of the solutions went from deep orange to various shades of red. Only when diazonium salts bearing strongly electron-donating groups (*e.g.*, *p*-methoxy) were used was the coupling reaction slow enough to permit partial hydrolysis of the protecting acetyl group, resulting in the formation of traces of other dyes. These impurities, whose presence could be detected in quite small amounts by paper chromatography, were removed during work-up of the hydrolysis reactions by taking advantage of their alkali solubility. One or two recrystallizations afforded products of analytical purity.

The 1-arylazo-2-naphthylamines (3) were similarly prepared in buffered aqueous acetic acid solution by the reaction of diazonium salts with β-naphthylamine. Melting points and analytical data for these compounds are reported in Tables I and II and the values of $\lambda_{\max}$ and extinction coefficients are given in Table III.

Two major effects were observed early in the course of preparing the dyes. Dyes of the type 7 (hereinafter referred to as series I), when compared to those of type 3 (series II) bearing the same substituent absorbed at about 60 ± 10 mμ longer wavelengths. The attachment of increasingly strongly electron-withdrawing groups to the benzene ring of both dye series produced a correspondingly increasing bathochromic shift of the visible absorption maximum. This latter observation led us to attempt to correlate the position of the absorption maxima with the Hammett sigma values.[6]

While many workers have correlated infrared absorption data with substituent constants,[7] there have also been a few reports of a similar treatment of visible absorption spectra. For example, Weissberger and co-workers[8] showed that the spectra of azomethine dyes (8), derived from substituted acylacetanilides by

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[5] This procedure was originally developed by Dr. T. W. Milligan of these laboratories.

[6] (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940; (b) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[7] For early references, see T. L. Brown, *ibid.*, **58**, 581 (1958).

[8] G. H. Brown, *et al.*, *J. Am. Chem. Soc.*, **79**, 2919 (1957).

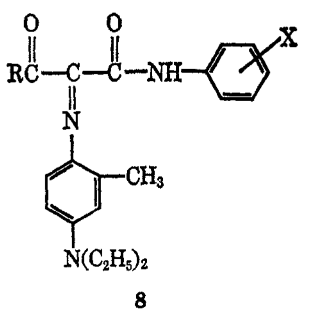
TABLE I

ANALYSES AND MELTING POINTS OF 7

		Analyses, %							
		C		H		N		Other	
X	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
p-NO$_2$	231–232^a	62.33	62.12	3.92	3.76	18.17	18.14		
m-NO$_2$	260–261^a		62.47		4.10		18.08		
p-CN	233–236	70.82	70.79	4.20	4.23	19.44	19.38		
m-CN	231–232^a		70.48		4.41		19.15		
p-CH$_3$CO	203–204	70.80	70.77	4.95	4.93	13.76	13.74		
m-CH$_3$CO	244.5–245.5^a		70.80		5.02		13.78		
m-CH$_3$SO$_2$	220–222^b	59.81	59.81	4.43	4.53	12.31	12.44	S, 9.39	9.25
p-CF$_3$	212.5–213.5	61.63	61.81	3.65	3.80	12.68	12.86	F, 17.20	17.55
m-CF$_3$	244–245		61.55		3.71		12.68		17.21
p-Br	209–210	56.16	56.19	3.54	3.41	12.28	12.37	Br, 23.35	23.31
m-Br	245–246^a		56.26		3.77		12.17		23.17
p-Cl	204–206	64.54	64.22	4.06	4.37	14.11	14.23	Cl, 11.91	11.77
m-Cl	234–235^a		64.59		4.00		14.36		11.92
p-I	212–213	49.38	49.13	3.11	3.42	10.80	10.63	I, 32.61	32.77
m-I	250–251^a		49.40		3.42		10.75		32.41
p-F	185–186	68.32	68.30	4.30	4.34	14.94	14.89	F, 6.75	6.78
m-F	211–212		68.34		4.08		15.03		6.67
p-C$_6$H$_5$	201–202	77.85	77.93	5.05	5.13	12.38	12.41		
m-C$_6$H$_5$	217–218		77.59		5.32		12.04		
p-CH$_3$CONH	249–250	67.48	67.54	5.03	4.92	17.49	17.57		
m-CH$_3$CONH	223–224		67.05		5.40		17.26		
β-C$_{10}$H$_7$	234–235^a	76.66	76.55	4.83	4.92	13.41	13.58		
p-C$_2$H$_5$O	134–135	70.34	70.17	5.58	5.74	13.67	13.63		
m-C$_2$H$_5$O	210–210.5		70.42		5.47		13.60		
p-CH$_3$S	180–181^c	66.00	66.05	4.89	5.14	13.58	13.57	S, 10.36	10.15
m-CH$_3$S	211–212^d		65.89		4.96		13.51		10.16
p-CH$_3$O	130–131	69.61	69.46	5.15	5.26	14.33	14.53		
m-CH$_3$O	216–217.5^a		69.78		5.36		13.96		
p-C$_2$H$_5$	179–181^e	74.20	74.33	5.88	5.76	14.42	14.51		
m-C$_2$H$_5$	171–171.5		74.12		5.97		14.38		
p-CH$_3$	179–179.5	73.63	73.71	5.45	5.38	15.15	15.21		
m-CH$_3$	196–198		73.83		5.25		15.29		
p-NH$_2$	281.5–283.0^f	69.05	69.17	5.07	5.01	20.13	20.32		
m-NH$_2$	165–167		69.21		4.93		20.27		
p-CH$_3$NH	183–184	69.84	69.84	5.52	5.65	19.17	19.03		
p-SF$_5$	250–251.5^g	49.36	49.44	3.11	3.20	10.79	10.84	F, 24.40	24.30
m-SF$_5$	231.5–232.5^e		49.21		3.09		10.67		24.35
H	156–157^h	72.98	72.90	4.98	5.16	15.96	15.84		

Recrystallization solvents follow (unless otherwise designated, compounds were recrystallized from ethanol). ^{a} Methoxyethanol. ^{b} n-Propyl alcohol. ^{c} Toluene. ^{d} Methanol. ^{e} Methylcyclohexane. ^{f} Carbon tetrachloride. ^{g} Isopropyl alcohol. ^{h} This compound was obtained in two forms, one of mp 156–157° when recrystallized from methylcyclohexane and one of mp 176–177° (*cf.* mp 176°, ref 4) when recrystallized from aqueous alcohol as reported in ref 4. Both forms gave correct elemental analyses.

oxidative coupling with a p-diethylaminoaniline, correlated with the σ constants for substituents on the anilide ring. Heilbronner[9] found that the spectral shifts ($\nu_x - \nu_h$, ν in cm^{-1}) of the principal visible absorption band of 1-arylazoazulenes (**9**) correlated with the



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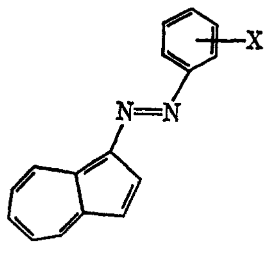

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absolute value of σ. In general, it would be anticipated that substituents with increasing electron-withdrawing or -donating properties would cause an increasing shift in the spectra of these dyes if the following assumptions were valid: that the absorption of light in this spectral region brings about a $\pi \rightarrow \pi^*$ transition from a ground state, in which the π electron system was *relatively* insensitive to changes in substituent, to an excited state which has considerable charge-separation character; and that the energy or the charge delocalization of this excited state is appreciably influenced by the electronic effects of the substituents.

Procedure and Results

Spectra for both series of dyes were determined in benzene and methylcyclohexane solution. As can be seen from Figures 1–4, the absorption spectra of these dyes do not give symmetrical curves and appear to exhibit, in favorable cases, three closely spaced maxima for dyes in series II, and two maxima for the 8-hydroxy analogs. These maxima have a spacing of about 900–1200 cm^{-1} which is reminiscent of the vibrational fine structure of the spectra of polycyclic hydrocarbons.

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[9] F. Gerson and E. Heilbronner, *Helv. Chim. Acta*, **42**, 1877 (1959).

TABLE II

ANALYSES AND MELTING POINTS OF **3**

		Analyses, %							
		C		H		N		Other	
X	Mp, °C[a]	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
p-NO_2	187–188[b] (180)[c]								
m-NO_2	184–185[d] (182)								
p-CN	189.5–190.0[e]	74.98	74.71	4.44	4.52	20.58	20.91		
m-CN	161–162[d]		74.96		4.55		20.94		
p-CH_3CO	181–183	74.72	74.84	5.23	5.40	14.53	14.72		
m-CH_3CO	172.5–174.5[e]		74.70		5.34		14.63		
p-C_2H_5OCO	134–138	71.45	71.37	5.37	5.43	13.16	13.02		
m-CH_3SO_2	168–170[e]	62.75	62.58	4.65	4.67	12.91	12.87	S, 9.85	9.92
p-CF_3	128.5–130	64.76	64.82	3.84	3.78	13.32	13.41	F, 18.08	18.17
m-CF_3	113.5–116		64.70		3.71		13.38		18.01
p-Cl	112.5–114.0 (116)								
m-Cl	95–96 (160, *sic.*)	68.21	68.07	4.29	4.17	14.91	14.97	Cl, 12.58	12.55
p-I	166–168 (170)								
m-I	130.5–131	51.49	51.30	3.24	3.43	11.26	11.09	I, 34.00	34.12
p-F	117.5–119.5 (120)								
m-F	81–83 (85)								
p-Br	132–134 (135)								
p-C_6H_5	197–198[d]	81.71	81.66	5.30	5.21	13.00	13.09		
m-C_6H_5	102–103.5		81.76		5.63		12.95		
p-CH_3CONH	213–214[e]	71.03	70.95	5.30	5.49	18.45	18.42		
m-CH_3CONH	129.5–130.5[b]		71.27		5.38		18.39		
β-$C_{10}H_7$	149–149.5 (149)								
p-C_2H_5O	134–135	74.20	74.08	5.88	5.80	14.42	14.57		
m-C_2H_5O	97–98		74.43		5.68		14.64		
p-CH_3S	118–119.5[e]	69.60	69.47	5.15	5.12	14.32	14.19	S, 10.93	10.96
m-CH_3S	97–98		69.67		5.10		14.04		10.54
p-CH_3O	124–125 (132–133)								
m-CH_3O	102–103	73.63	73.51	5.45	5.61	15.15	15.32		
p-C_2H_5	92–93	78.51	78.83	6.22	6.38	15.26	15.02		
m-C_2H_5	49.0–49.5		78.38		6.19		15.23		
p-CH_3	111.5–113.0 (114)								
m-CH_3	99.5–101.5 (103–104)[d]								
p-NH_2	154–155[e]	73.26	73.30	5.38	5.56	21.36	21.42		
m-NH_2	124.5–125.5		73.26		5.44		21.13		
p-CH_3NH	112.5–113.5[e]	73.89	73.74	5.84	5.77	20.28	20.53		
p-C_6H_5CO	178.5–179.5[d]	78.61	78.61	4.88	5.02	11.96	11.87		
p-SF_5	142–143	51.47	51.43	3.24	3.20	11.25	11.17	F, 25.44	25.38
m-SF_5	141–142.5[f]		51.47		3.27		11.22		25.49
H	103.5–104.5 (103)								

[a] Recrystallization solvent was hexane with the exceptions noted. [b] Benzene. [c] Melting points in parentheses are those reported by H. H. Hodgson and C. K. Foster [*J. Chem. Soc.*, 30 (1942)] unless otherwise designated. [d] G. M. Norman, *ibid.*, **101**, 1913 (1912). [e] Ethanol. [f] Cyclohexane.

Because of these irregularities of curve shape and the uncertainties in assigning precise values to the absorption maxima, values used in the correlation with σ represent the midpoint of the horizontal line drawn at half-band height,[10] determined on curves plotted on a linear optical density vertical scale using solutions of an optical density of 1.5. These values were found to be independent of the optical densities at which the curves were measured (within the range of *ca* 0.7–1.7) and were reproducible within ±1 mμ among several determinations or observers. These values and the values of sigma used in this work are given in Table IV.

When the spectral data from both series of dyes were plotted *vs.* sigma values, both using values of λ in mμ obtained as described above and of $10^3/\lambda$ (which is directly proportional to the transition energy),[11] there was, for the dyes bearing substituents with positive values of σ, a smooth dependence of the data on σ. It was also found that the special sigma values, assigned to several strongly electron-withdrawing *para* substituents for use in the study of certain reactions of anilines and phenols involving charged transition states,[6b] designated σ^*, were required for the *p*-nitro, *p*-cyano, and *p*-acetyl groups. In addition, by substituting one or the other of the two possible values of each σ constant in a series of least-square calculations[6b] and examining the resulting change in the correlation coefficient, it was found that, while the carbethoxy group also required σ^*, the trifluoromethyl group did not. The fact that a σ^* value for the *p*-trifluoromethyl

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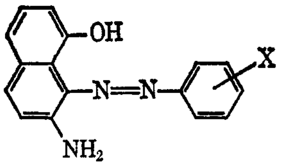
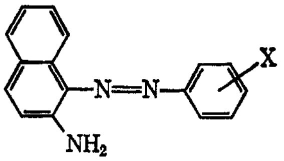
(10) Ideally, one should like to be able to use a value which corresponds to the 0 → 0 transition of the dye for this work. These values are usually obtained by measuring absorption spectra of solutions of dyes in a frozen matrix at low temperatures, a procedure difficult to apply, especially to the study of a large number of compounds. The numbers used here represent a 0 → 0 transition weighted by a set of vibrational subtransitions whose intensities are presumably governed by the Franck–Condon principle and whose distribution and relative intensities we must assume are more or less the same throughout a given dye series.

(11) Within the small range of values considered here, $|\Delta\nu|$ is proportional to $|\Delta\lambda|$ and, as is shown in Table V, the values of λ and $10^3/\lambda$ correlate equally well with σ.

TABLE III

VISIBLE ABSORPTION SPECTRA[a]





Substituent	Benzene		Methylcyclohexane		Benzene		Methylcyclohexane	
	λ_{max}, mμ	$\epsilon_{max} \times 10^{-4}$	λ_{max}, mμ	$\epsilon_{max} \times 10^{-4}$	λ_{max}, mμ	$\epsilon_{max} \times 10^{-4}$	λ_{max}, mμ	$\epsilon_{max} \times 10^{-4}$
p-NO_2	547	2.12	...	...	496	1.86	486	1.88
p-CN	529	1.86	...	...	480	1.78	472	1.68
p-CH_3CO	530	1.92	...	...	477	1.78	469	1.72
p-C_2H_5OCO	...	...	...	...	471	1.68	462	1.66
p-CF_3	519	1.62	521	1.56	462	1.40	455	1.39
p-I	517	1.92	517	1.88	463	1.66	456	1.60
p-Br	510	1.82	512	1.80	460	1.66	450	1.56
p-Cl	510	1.76	512	1.80	457	1.44	450	1.48
p-F	506	1.46	502	1.32	450	1.40	437	1.30
p-C_6H_5	517	2.26	516	2.14	457	1.38	450	1.82
H	509	2.48	...	...	439	1.36	430	1.34
p-CH_3CONH	511	2.09	...	...	460	1.86	...	...
p-CH_3S	519	2.20	...	...	467	1.92	458	1.88
p-C_2H_5	504	1.76	501	1.68	440	1.38	431	1.55
p-CH_3	503	1.67	501	1.62	440	1.40	429	1.46
p-C_2H_5O	504	1.96	502	1.98	450	1.62	444	1.66
p-CH_3O	503	1.92	500	1.80	449	1.51	443	1.52
p-CH_3NH	513	2.86	507	2.25	467	2.44	455	2.14
p-NH_2	509	2.48	...	...	458	1.96	450	1.78
m-NO_2	520	1.50	...	...	470	1.42	461	1.52
m-CN	518	1.66	...	...	466	1.40	458	1.48
m-CF_3	515	1.60	516	1.35	460	1.38	452	1.40
m-I	515	1.72	513	1.48	460	1.50	453	1.44
m-Br	515	1.58	515	1.48	...	...	...	...
m-Cl	511	1.64	513	1.44	460	1.40	449	1.38
m-F	512	1.59	512	1.54	456	1.36	450	1.34
m-CH_3CO	511	1.60	...	...	456	1.42	446	1.46
m-C_6H_5	508	1.66	507	1.54	450	1.36	434	1.46
m-CH_3CONH	507	1.62	...	...	450	1.38	440	1.40
m-C_2H_5O	506	1.69	502	1.58	449	1.38	434	1.44
m-CH_3S	510	1.68	507	1.56	450	1.38	439	1.40
m-CH_3O	507	1.67	503	1.45	446	1.34	432	1.38
m-C_2H_5	502	1.64	500	1.56	438	1.36	431	1.32
m-CH_3	504	1.60	502	1.53	439	1.30	430	1.38
m-NH_2	508	1.72	...	...	440	1.40	432	1.48
β-$C_{10}H_7$	517	2.26	513	2.10	460	1.90	452	1.80
p-SF_5	524	1.66	526	1.60	468	1.48	462	1.46
m-SF_5	516	1.60	518	1.50	465	1.40	458	1.40
p-C_6H_5CO	...	...	...	...	480	1.80	470	1.76
m-CH_3SO_2	518	1.64	...	...	466	1.44	...	...

[a] In all cases, values of λ_{max} and ϵ given are for the true absorption maximum. In those cases (*cf.* Figures 1 and 2) where more than one band was clearly resolved, the values given here are for the most intense absorption band. These values of λ_{max} are *not* those used in the correlations with substituent constants; see Table IV.

group is not required for these dyes suggests that for this substituent, hyperconjugative resonance of the type suggested by Roberts[12] does not occur here.

Inspection of plots of the data showed that the spectral values for the substituents with negative σ values did not follow the same trend as the rest of the set. Calculations using just the negative sigma points showed no statistically significant slope and thus it was felt that the inclusion of these points either in the complete calculations or in a correlation with the absolute value of σ[9] could not be reasonably justified. Data for the *p*-phenyl and *β*-naphthyl groups were also omitted from the calculations. Inasmuch as the absorption of light by these chromophores involves excitation of the entire π system, the attachment of an additional aromatic ring either in the *para* position, or fused to the 3,4 position (*i.e.*, *β*-naphthyl) would be expected to have an anomalously large effect.

With these exclusions, calculations of rho, which gave correlation coefficients of >0.95, were performed for the remaining 22 points in each of the two dye sets determined in benzene and, in addition, for the 1-arylazo-2-naphthylamines determined in methylcyclohexane (a number of the series I dyes were insufficiently soluble in methylcyclohexane to permit accurate determination of their wavelengths). In addition, the values for the positive *meta* and *para* substituents were separated one from the other and each group

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(12) J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950).

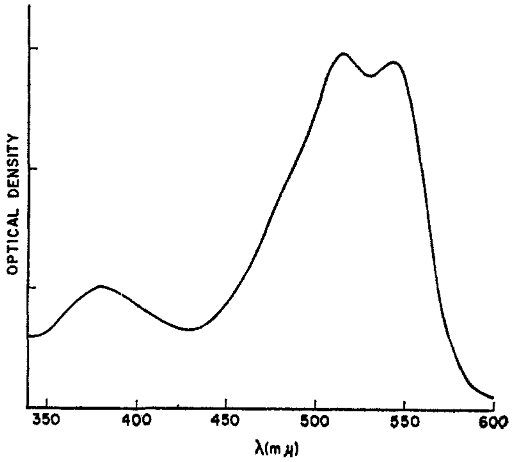


Figure 1.—Absorption spectrum of 1-(p-methylaminophenylazo)-2-amino-8-naphthol (7, X = p-CH$_3$NH) in benzene.

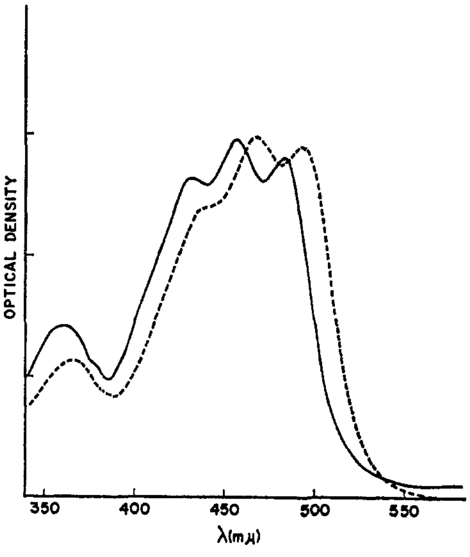


Figure 2.—Absorption spectrum of 1-(p-methylaminophenylazo)-2-naphthylamine (3, X = p-CH$_3$NH): ———, in methylcyclohexane; ----, in benzene.

was individually correlated with sigma to give different values of rho.

Similarly, the values for the *meta*- and *para*-substituted dyes were correlated with the sigma values proposed by Taft[13] for the separate examination of inductive and resonance effects to give correlation coefficients of *ca.* 0.87–0.90. For these latter calculations, all of the data for which the corresponding sigma values were available were used except for the p-amino group. The numerical results of the calculations are given in Table V, and examples of the graphical results of plotting wavelength *vs.* sigma are shown in Figures 5 and 6.

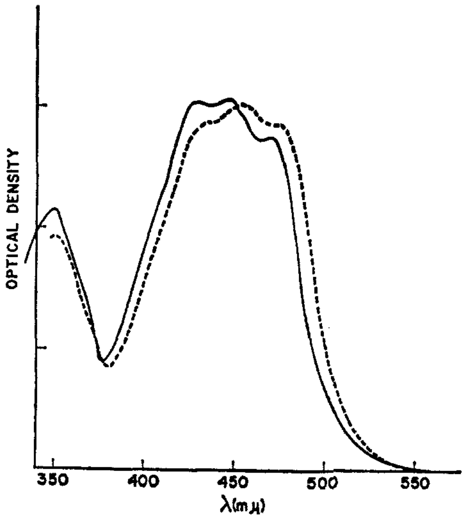


Figure 3.—Absorption spectrum of 1-(p-methoxyphenylazo)-2-naphthylamine (3, X = p-CH$_3$O): ———, in methylcyclohexane; ----, in benzene.

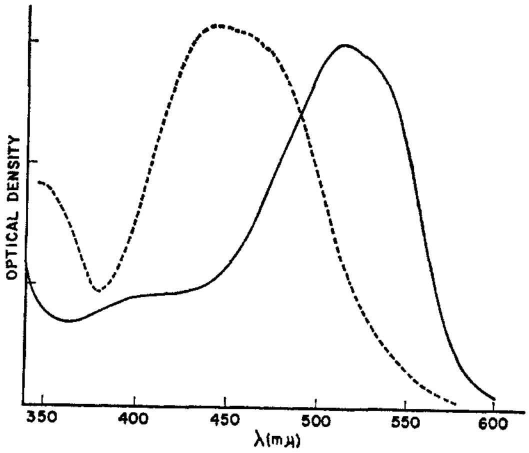
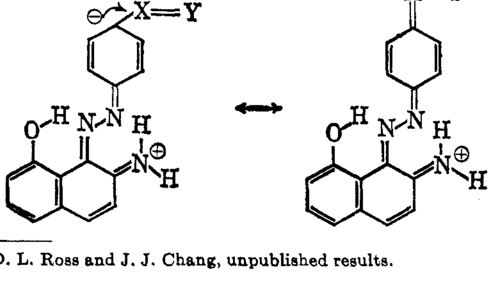


Figure 4.—Absorption spectra in benzene for 1-(m-trifluoromethylphenylazo)-2-amino-8-naphthol (7, X = m-CF$_3$) (———), and 1-(m-trifluoromethylphenylazo)-2-amino-8-naphthyl acetate (6, X = m-CF$_3$), ----.

Discussion

The fact that there is good correlation between sigma and position of absorption band for the dyes bearing electron-withdrawing substituents supports the supposition that these substituents have an electronic effect on the excited state of the dye molecule analogous to the electronic effects they have on the reactivities of substituted benzene derivatives. Those substituents which aid in the stabilization of negative charge distributed on the benzene ring, either by resonance or inductive effects, will correspondingly lower the energy of the excited state, and therefore cause the transition to occur at longer wavelenth. This conclusion is supported by the observation[14] that dyes analogous to 7 in which the 2-amino group is replaced by the more strongly electron-donating methylamino group absorb at *ca.* 15 mμ longer wavelengths. (See Chart II.)

In analogy with the postulated resonance structures for intermediates involving reactions of substituted anilines for which σ^* values are required, substituents of the type $-X{=}Y$ (*e.g.*, NO$_2$, C$\equiv$N, O$=$CR), when placed at the *para* position lengthen the conjugating system by one double bond as shown below.



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

(14) D. L. Ross and J. J. Chang, unpublished results.

CHART II

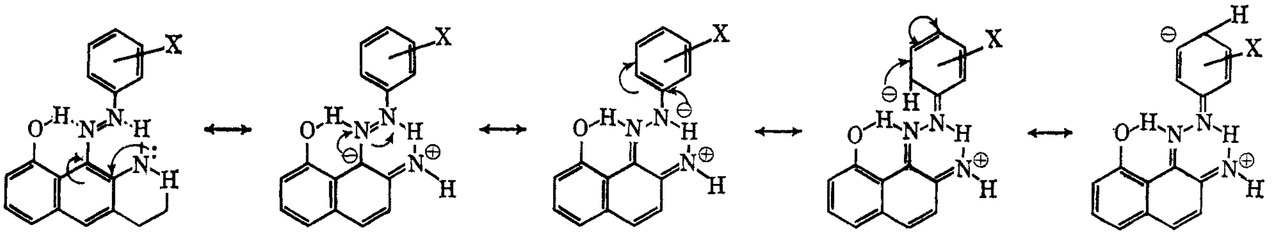


TABLE IV

VALUES OF λ, σ, σ_I, AND σ_R USED

	λ (mμ)[a]					
		Series II				
Substituent	Series I, benzene	Benzene	Methylcyclohexane	σ[b]	σ_I[c]	σ_R[c]
p-NO_2	546	491	470	+1.270		+0.64
p-CN	531	472	468	+1.00		+0.41
p-CH_3CO	528	471	463	+0.87		+0.60
p-C_6H_5CO	...	472	465	...		...
p-SF_5	521	464	458	...		...
p-C_2H_5OCO	...	466	459	+0.678		+0.358
p-CF_3	516	458	453	+0.551		+0.130
p-I	516	458	453	+0.276		−0.10
p-Br	512	455	451	+0.232		−0.22
p-Cl	512	453	448	+0.226[d]		−0.24
p-F	504	444	441	+0.062		−0.46
p-C_6H_5	518	458	451	−0.009		−0.11
H	502	446	439	0.00		0.00
p-CH_3CONH	513	454	...	−0.015		−0.28
p-CH_3S	518	460	452	−0.047		−0.297
p-C_2H_5	503	446	440	−0.151		...
p-CH_3	503	444	440	−0.170		−0.12
p-C_2H_5O	505	447	440	−0.250		...
p-CH_3O	505	445	440	−0.268		−0.52
p-CH_3NH	518	461	449	−0.592		...
p-NH_2	510	453	443	−0.660		−0.76
m-NO_2	520	463	458	+0.710	+0.63	
m-CN	517	459	456	+0.678	+0.59	
m-CH_3SO_2	518	461	454	+0.647	+0.59	
m-SF_5	...	458	453	...	...	
m-CF_3	512	455	451	+0.415	+0.41	
m-Br	512	...	...	+0.391	+0.45	
m-Cl	512	454	448	+0.373	+0.47	
m-I	513	457	450	+0.352	+0.39	
m-F	510	454	447	+0.337	+0.52	
m-CH_3CO	510	454	446	+0.306	+0.27	
m-C_6H_5	507	449	444	+0.218	+0.10	
m-CH_3CONH	507	450	444	+0.210[e]	+0.28	
m-C_2H_5O	507	449	442	+0.150	...	
m-CH_3S	509	450	444	+0.144	+0.25	
m-CH_3O	506	448	442	+0.115	+0.25	
m-C_2H_5	512	446	439	−0.043	...	
m-CH_3	505	445	438	−0.069	−0.05	
m-NH_2	508	447	440	−0.161	+0.10	
β-$C_{10}H_7$	516	459	450	+0.170	...	

[a] Represents midpoint of half-band height when visible absorption band plotted as optical density *vs.* wavelength at optical density = 1.5. [b] Values of the Hammett sigma constants taken from ref 6b unless otherwise noted. [c] Values of σ_I and σ_R taken from ref 13 and C. N. R. Rao and C. K. Goldman, *Can. J. Chem.*, **36**, 1596 (1958). [d] Value from J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956. [e] Value from D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

That this enhanced conjugation is taking place is supported by the increase in extinction coefficient seen for those dyes bearing the σ* substituents. Since the extinction coefficient is proportional to the square of the change in dipole moment on going from the ground to excited state, an increase in distance of charge separation will be reflected in a higher value of ε.

From the plots of the data *vs.* the sigma values of Taft[13] for inductive (σ_I) and resonance (σ_R) effects (Figure 6), it is seen that values for the *meta*-substituted compounds show an even trend with little scatter. The calculated line passes through the value for the unsubstituted dye. These substituents clearly influence the energy of the transition by simple inductive effects. The plot of values for the *para*-substituted dyes *vs.* the resonance sigma values has a higher rho value, suggesting that the transition energy is more strongly influenced by resonance effects than by

TABLE V

RESULTS OF LEAST-SQUARES CORRELATIONS OF DYE ABSORPTION SPECTRA WITH σ VALUES

Dye series[a]	Solvent[b]	Sigma[c]	vs. λ			vs. $1/\lambda \times 10^3$			Value for unsubstituted dye			
									Calcd[f]		Found	
			ρ	r[d]	s_ρ[e]	ρ	r[d]	s_ρ[e]	λ	$1/\lambda \times 10^3$	λ	$1/\lambda \times 10^3$
I	Benzene	σ	29.44	0.96	2.02	−0.1081	0.96	0.0072	502.1	1.9893	502	1.992
I	Benzene	σ_I	19.63	0.87	3.06	−0.0748	0.87	0.0115	504.3	1.9821	502	1.992
I	Benzene	σ_R	27.79	0.87	4.64	−0.1021	0.88	0.0170	518.3	1.9300	502	1.992
II	Benzene	σ	31.08	0.95	2.19	−0.1443	0.96	0.0097	443.8	2.2497	446	2.242
II	Benzene	σ_I	23.69	0.91	3.17	−0.1160	0.91	0.0153	445.1	2.2461	446	2.242
II	Benzene	σ_R	29.42	0.88	4.68	−0.1369	0.88	0.0215	459.6	2.1767	446	2.242
II	Mch	σ	24.88	0.96	1.60	−0.1198	0.96	0.0079	440.3	2.2692	439	2.278
II	Mch	σ_I	26.21	0.91	3.36	−0.1308	0.92	0.0166	438.3	2.2808	439	2.278
II	Mch	σ_R	22.94	0.90	3.35	−0.1107	0.90	0.0165	452.9	2.2092	439	2.278
I	Benzene	σ_m	21.69	0.97	1.66	−0.0821	0.97	0.0064	503.8	1.9841	502	1.992
I	Benzene	σ_p	29.97	0.97	2.92	−0.1092	0.97	0.0103	503.8	1.9826	502	1.992
II	Benzene	σ_m	22.72	0.96	2.02	−0.1104	0.96	0.0098	445.9	2.2420	446	2.242
II	Benzene	σ_p	32.17	0.96	3.44	−0.1478	0.96	0.0153	444.6	2.2454	446	2.242
II	Mch	σ_m	25.32	0.98	1.55	−0.1247	0.98	0.0078	439.1	2.2761	439	2.278
II	Mch	σ_p	22.44	0.97	2.25	−0.1073	0.96	0.0114	443.3	2.2546	439	2.278

[a] Series I and II designate dyes of structures **7** and **3**, respectively. [b] Mch designates methylcyclohexane. [c] σ is the Hammett sigma constant; the calculations included only those dyes with positive sigma substituents, *p*-phenyl and β-naphthyl excluded; σ_I and σ_R are the Taft sigma constants; the calculations included all dyes for which the sigma values were available except *p*-amino; σ_m and σ_p are the positive Hammett sigma values for *meta* and *para* substituents, the value for *p*-phenyl was excluded from the calculations using σ_p. [d] The correlation coefficient; see ref 6b. [e] The standard deviation of rho. [f] These are the calculated values of the constant in the expressions λ = constant + $\rho\sigma$ and $1/\lambda \times 10^3$ = constant + $\rho\sigma$.

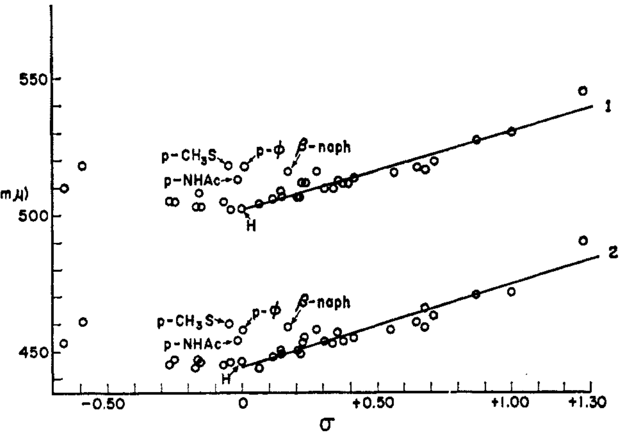


Figure 5.—Plots of λ *vs.* Hammett σ values for half-band height midpoints as determined in benzene solution. Upper curve for series I dyes (**7**), lower curve for series II dyes (**3**).

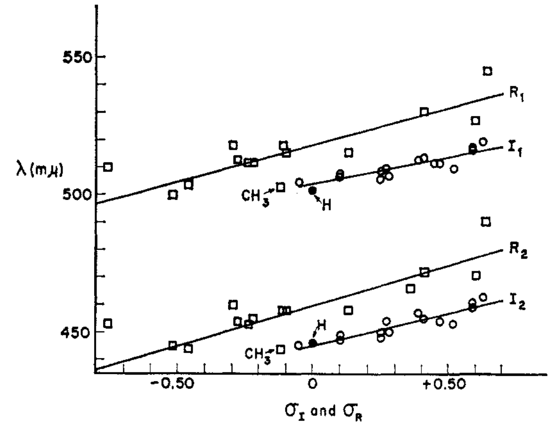
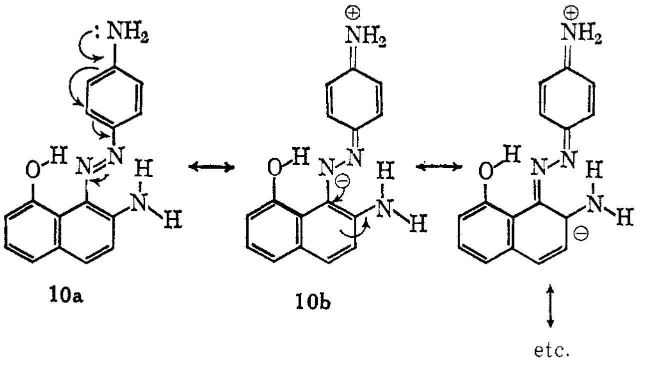


Figure 6.—Plots of λ *vs.* Taft σ values for resonance (σ_R, squares) and inductive (σ_I, circles) effects for half-band height midpoints determined in benzene solution using, respectively, the *para-* and *meta*-substituted dyes of series I (upper pair of lines) and series II (lower pair of lines).

inductive effects. It also accommodates two substituents which appeared to be anomalous when plotted *vs.* the conventional Hammett sigma values, namely *p*-phenyl and *p*-acetamido. The dyes bearing these two substituents were omitted from our calculations of rho for the Hammett plot because of the wide deviation of their wavelengths from the expected values. Inasmuch as resonance effects are more important than inductive effects here, the Hammett value for the *p*-acetamido group (−0.015), which reflects a nullifying compromise between opposing inductive and resonance effects, does not adequately describe the influence of this substituent.

The fact that the values for all of the *para*-substituted dyes fall reasonably well on the σ_R plot [with the exception, other than the two extremes, of *p*-methyl and *p*-methylmercapto (see below)] indicates that the resonance structures for charge separation in the excited state shown above do not present a complete description of the system. It is clear that the electron-*donating para* substituents are also strongly interacting with the π system in the excited state. The extinction coefficients for dyes with such substituents as *p*-methoxy and *p*-acetamido are enhanced, while those for *p*-amino and *p*-methylamino are higher even than the value of the *p*-nitro compound. Thus, charge separation in the opposite sense from that shown above must also play a role in the excited state. The large deviation of the *p*-methyl compounds toward wavelengths



10a **10b**

shorter than predicted by its σ_R value is interesting. Presumably, if p-CH_3 were to have a resonance effect, it would do so as a result of hyperconjugation. As in the case of the trifluoromethyl group discussed above, this effect does not appear to take place in these systems.

While the σ_R plots accommodate the values for iodo, bromo, and chloro, these substituents produce absorptions that are somewhat more bathochromic than their Hammett values would predict. The extinction coefficients are 2000–4000 units higher than the corresponding *p*-fluoro derivatives, suggesting considerable resonance effects. Similarly, the *p*-methylmercapto-substituted dyes are considerably more bathochromic than even the σ_R value of this group would predict and show very high extinction coefficients. We believe that these four substituents show these enhancements because of significant d-orbital participation[15] in the electronic configuration of the excited state. An effect of this magnitude for the methylmercapto group appears to be unique to these systems.[16]

Thus far we have discussed features which are characteristic of both sets of dyes. Indeed, except for the shift to longer wavelength on introduction of the hydroxyl group in the 8 position, the effects of substituent on absorption spectrum in the two sets of dyes are completely parallel. On the basis of the insolubility of series I dyes in alkali and the insensitivity of their solution absorption spectra to changes in pH, it seems certain that the 8-hydroxy group is indeed involved in an extremely stable six-membered hydrogen bonded ring with the α-azo-nitrogen atom. We believe that the principal effect of the *peri*-hydroxyl group is that it serves, through hydrogen bonding, in conjunction with a similar role played by the 2-amino group, to lock the azo group into a configuration in which it achieves maximum coplanarity with the naphthalene ring. This serves to lower the energy of excitation of the molecule and, at the same time to increase the transition probability, an effect reflected in the higher extinction coefficients of this dye system as compared with those of the 1-arylazo-2-naphthylamines. The greater sensitivity of the extinction coefficients of series I dyes to change in substituent may be a result of the higher degree of coplanarity attained by these compounds.

That the role of the 8-hydroxyl group is *not* principally an electronic one is demonstrated by comparing (Figure 4) the absorption spectra of 8-acetoxy-1-(*m*-trifluoromethyl)phenylazo-2-naphthylamine (**6**, X = *m*-CF_3), λ_{max} 437 mμ (ϵ 9400), with the 8-hydroxy compound, λ_{max} 515 mμ (ϵ 15,800). Here the spectrum is shifted to an even shorter wavelength than that of the 2-naphthylamine derivative (λ_{max} 460 mμ, ϵ 13,800). If the 8 substituent were having a significant electronic effect on the transition, an intermediate wavelength would be expected. The lower ϵ_{max} of the 8-acetoxy compound presumably is due to the bulk of the substituent forcing the azo group out of the plane of the naphthalene ring. If an interaction involving oxygen-to-nitrogen hydrogen transfer in resonance structure **10b** were important, one would expect a difference between series I and II in the wavelength dependence of dyes bearing electron-donating substituents. It is interesting to note that the average increase in wavelength of 58 mμ on going from series II to series I corresponds to a net decrease of the transition energy of *ca.* 7 kcal, a representative value to be expected for a hydrogen bond.

As a test for the possible utility of the λ *vs.* σ relations calculated from our data for predicting sigma values for new substituents, we prepared dyes bearing the *m*- and *p*-pentafluorosulfur group recently reported by Sheppard[17] and also dyes with the *p*-benzoyl group, whose σ^* value has not been reported. Using the procedure of Jaffé[6b] for calculating sigma values, and the values of rho from our results of correlating separately the positive *meta* and *para* substituents *vs.* λ (since these gave the highest correlation coefficients), we arrived at values of $+ 0.57 \pm 0.11$ and 0.54 ± 0.04 for the *p*- and *m*-SF_5 groups (which are somewhat lower than those reported by Sheppard[18] and indicate that, again, no σ^* value is required for the *p*-SF_5 group for these dyes), and a value of $+0.94 \pm 0.11$ for the *p*-benzoyl group, which is close to the value of $+ 0.87$ used as σ^* for the *p*-acetyl group.

Experimental Section[19]

1-Acetoxy-7-naphthylamine Hydrochloride (5).—A solution of 4.78 g of 7-amino-1-naphthol[20] in 50 ml of glacial acetic acid was saturated with gaseous hydrogen chloride at room temperature over a period of 30 min. Acetyl chloride (10 ml) was added, and, with the continuous introduction of a slow stream of hydrogen chloride, the temperature was raised to 40° and maintained at 40–45° for 45 min. In some instances the product precipitated during this period. The mixture was cooled to room temperature and poured into 100 ml of dry ether. The product, a pale grey solid, was collected by suction filtration, washed with ether, and dried to give 5.88 g (87.5%), mp 198.6–200° dec. An analytical sample, prepared by recrystallization from ethanol or isopropyl alcohol, had mp 210–211° dec.

Anal. Calcd for $C_{12}H_{12}NO_2Cl$: C, 60.64; H, 5.09; N, 5.89; Cl, 14.92. Found: C, 60.79; H, 5.07; N, 6.16; Cl, 14.70.

Substituted Anilines.—With the exceptions noted below, these were purchased from Distillation Products Industries, Aldrich Chemical Company, Inc., Pierce Chemical Company, or Chemicals Procurement Laboratories, Inc. Catalytic reduction of 3-nitrobiphenyl and 3-nitrobenzonitrile gave the corresponding amino compounds. Acetylation of 3-methylmercaptoaniline followed by oxidation and hydrolysis gave methyl-3-aminophenyl sulfone. We are indebted to Dr. William A. Sheppard of the Central Research Department, E. I. du Pont de Nemours and Company for samples of *m*- and *p*-aminophenylsulfur pentafluoride hydrochlorides.

1-Arylazo-2-amino-8-naphthols were prepared as illustrated by the following procedure.

1-(*p*-Acetamido)phenylazo-2-amino-8-naphthol (11).—A solution of 0.60 g of *p*-aminoacetanilide in 1.5 ml of concentrated hydrochloric acid, 7 ml of glacial acetic acid, and 6 ml of water was cooled to 0–5°. A solution of 0.28 g of sodium nitrite in 2 ml

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(15) *Cf.* R. W. Taft, Jr., *J. Chem. Phys.*, **26**, 93 (1957); H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

(16) In this connection, it is of interest to compare the work of J. E. Bloor and D. B. Copley [*Chem. Ind.* (London), 526 (1960)], who calculated a number of "empirical spectroscopic substituent constants" for fitting the electronic absorption spectra of a set of *para*-substituted nitrobenzenes to a Hammett-type plot. Their calculated constants for iodo (0.53) and CH_3S (0.90) are considerably larger than the conventional Hammett values (0.276 and −0.047, respectively) as is their value for CH_3CONH (0.64 *vs.* −0.015), indicating that these groups have effects on the nitrobenzene spectra similar to those discussed here.

(17) W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3064 (1962).

(18) W. A. Sheppard, *ibid.*, **84**, 3072 (1962).

(19) Melting points are uncorrected and were obtained on a Mel-Temp capillary melting point apparatus. Elemental analyses were by Dr. S. M. Nagy of the Microchemical Laboratory, Massachusetts Institute of Technology, and by Alfred Bernhardt, Mülheim, Germany. Quantitative visible spectra were determined on 5×10^{-5} *M* solutions in the appropriate solvents using a Cary Model 11 spectrophotometer.

(20) A. C. Mueller and C. S. Hamilton, *J. Am. Chem. Soc.*, **66**, 860 (1944).

of water was added dropwise with stirring, the temperature of the solution being kept below 5° with an ice bath. Stirring was continued for 5–10 min after addition of the sodium nitrite and then any excess nitrous acid was destroyed (starch–iodide test paper) by the addition of small portions of sulfamic acid.

The diazonium solution was added to a stirred solution of 0.95 g of **5** in 50 ml of 80% acetic acid at room temperature. The pH of the coupling mixture was brought to 4–5 by the addition of saturated sodium acetate solution. An immediate orange color developed. The extent of coupling was followed by periodic spot tests of the solution with resorcinol and tetrazotized dianisidine ("Fast Blue B Salt"). Coupling was complete after 3 hr. The solution was diluted slowly with 100 ml of water and the orange precipitate was collected by suction filtration and washed with water.

With most of the diazonium salts used in this work, the coupling reaction was complete within 5 hr. In a few cases (diazotized *p*-anisidine and other anilines bearing electron-donating groups) where slow reaction was observed, the coupling mixture was allowed to stand overnight in a refrigerator before dilution with water.

The crude O-acetylated dye was dissolved in 50 ml of methoxyethanol and stirred at room temperature for 30 min with 5 ml of 20% sodium hydroxide solution. The color rapidly changed from orange to deep red. The solution was then diluted with 5–6 times its volume of water and the precipitate was collected, washed with water, dried, and recrystallized from 80 ml of ethanol to give 0.79 g (62%) of dark needles.

1-Arylazo-2-naphthylamines were prepared as illustrated by the following procedure.

1-(*p*-Acetamido)phenylazo-2-naphthylamine.—The solution prepared by diazotizing 1.50 g of *p*-aminoacetanilide in 10 ml of water, 15 ml of acetic acid, and 4.5 ml of concentrated hydrochloric acid at 0–5° with 0.70 g of sodium nitrite was added to a solution of 1.43 g of β-naphthylamine in 120 ml of 80% acetic acid. The pH of the solution was brought to 4–5 by the addition of saturated sodium acetate solution. After 4 hr, the solution was diluted with 200 ml of water. The precipitated dye was collected by suction filtration, washed with water, dried, and recrystallized from 75 ml of ethanol to give 2.38 g (78%) of minute orange needles.

1-(*m*- and *p*-amino)phenylazo-2-amino-8-naphthols and 1-(*m*- and *p*-amino)-2-naphthylamines were prepared by hydrolysis of the corresponding N-acetyl compounds as illustrated by the following procedure.

1-(*p*-Amino)phenylazo-2-amino-8-naphthol (10).—A solution of 1.60 g of **11** in 25 ml of methoxyethanol containing 10 g of 50% sodium hydroxide solution was heated at 80° for 25 min, on a steam bath. After cooling to room temperature, the solution was diluted with 150 ml of water. The precipitated dye was recrystallized from 500 ml of carbon tetrachloride to give 0.99 g (71%) of dark crystals.

1-(*m*-Trifluoromethyl)phenylazo-8-acetoxy-2-naphthylamine.—To a solution of 2.38 g of **5** in 150 ml of 80% aqueous acetic acid was added the solution prepared by diazotizing, at 0–5°, 1.6 g of *m*-aminobenzotrifluoride in 15 ml of acetic acid, 10 ml of water, and 4.5 ml of concentrated hydrochloric acid with 0.70 g of sodium nitrite dissolved in 3 ml of water. Coupling began immediately. The pH was brought to 4–5 by the addition of saturated sodium acetate solution. The dye began to separate in microcrystalline form. Water (250 ml) was added in small portions over a period of 40 min at which time the reaction was complete. The product was collected, washed with water, and, after being dried *in vacuo* over potassium hydroxide, weighed 3.23 g (86.5%), mp 117–118.5°. An analytical sample, recrystallized from cyclohexane, had mp 134–135°, λ_{max} (benzene) 437 mμ (ε 9400). (See Figure 4.)

Anal. Calcd for $C_{19}H_{14}N_3O_2F_3$: C, 61.13; H, 3.78; N, 11.26; F, 15.27. Found: C, 61.41; H, 4.15; N, 10.99; F, 15.01.

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Acetylenic Amines. XIII. Syntheses of 3-Carboxy-3-pyrrolin-2-ones

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A new synthesis of 3-carboxy-3-pyrrolin-2-ones XVIII from oxazolidines VII has been investigated. The oxazolidines are readily available from the condensation of 2-propynylamines V and malonic esters. The conversion of VII to XVIII with acid or base involves a β-ketoamide intermediate XV which on cyclization readily hydrolyzes and dehydrates to XVIII. A general method for making 3-substituted 3-pyrrolin-2-ones XXIV from N-(1,1-dialkyl-2-propynyl)acetamides XXII involving the ketoamide intermediate has been made available.

The acid-catalyzed cyclization of acetylenic amides I to the oxazolinium salts II, together with metal-catalyzed cyclization to the oxazolines III, has been reported.[1,2] (See Scheme I.)

Preliminary attempts to prepare IV by treatment of the amides I where R^2 is alkyl either with acid followed by anhydrous base or with a metallic catalyst were unsuccessful. Compounds with substitution such as carbethoxy on the 2-methylene group of IV, which should stabilize the oxazolidine structure thus facilitating its isolation, were chosen for an extension of this study. In order to obtain the appropriate α-carbethoxyacetamides VI for cyclization, the condensation of secondary 2-propynylamines with malonic esters was investigated.

The reaction of N,1,1-trimethyl-2-propynylamine (Va) and malonic ester gave a product which was assigned the oxazolidine structure VIIa since its infrared spectrum had multiple absorptions in the carbonyl region and no acetylenic hydrogen absorption in the 3.02-μ region. A study of the nmr spectrum[3] substantiated the oxazolidine structure. There were two doublets centered at 282 cps and 255 cps (*J* = 3 cps) assigned to the *gem*-vinyl protons. A singlet at 240 cps was assigned to proton on the vinyl group containing the carbethoxy group. The remaining peaks

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(1) N. R. Easton and R. D. Dillard, *J. Org. Chem.*, **28**, 2465 (1963).

(2) N. R. Easton, D. R. Cassady, and R. D. Dillard, *ibid.*, **30**, 3084 (1965).

(3) The machine used was the Varian Associates Model HR-60, 60 Mc. Deuteriochloroform was used as the solvent and tetramethylsilane as the internal reference.