

119($C_2F_4^+$), 31(CF^+), 50(CF_2^+), 100($C_2F_4^+$), 64(CF_2N^+), 114($C_2F_4N^+$), 45(CFN^+) and 109 ($C_2F_2N_2^+$). There was also a small peak at mass 197($C_2F_7N_2^+$), while the absence of peaks at 33 and 52 indicated that there was no N-F bonding in this compound.

Fluorinolyses.—1. When $CF_3N=NCF_3$ (0.04 mole/hr.) was allowed to react with fluorine (0.15 mole/hr.) in the jet reactor, the only products formed were CF_4 (15 parts), CF_3NF_2 (1 part) and $(CF_3)_2NF$ (1 part). At 150°, 10% of the $CF_3N=NCF_3$ was returned unchanged, while at 30°, 25% did not react. 2. When F_2 , $NF_2CF_2CF_2NF_2$ and nitrogen in the molar ratio 15:1:50 were introduced into the jet reactor at 200°, only 10% of the $NF_2CF_2CF_2NF_2$ underwent fluorinolysis to give CF_4 (1 part), NF_3 (2 parts), $CF_3CF_2NF_2$ (25 parts) and an unidentified compound (10 parts). The last mentioned had a very simple infrared spectrum with one absorption, a triplet, centered at 10.65 μ . 3. Fraction 2, Table V, which contained $(CF_3)_2NF$, $CF_3CF_2NF_2$, $CF_3N=NCF_3$, $(CF_3)_2N$, $CF_3NFC_2F_5$, $NF_2CF_2CF_2NF_2$ and $CF_3N=NC_2F_5$ was fluorinated at a molar reaction ratio of 3:1:8 at 200°. The product contained CF_4 and C_2F_6 with a little CF_3NF_2 as well as all of the original materials except $CF_3N=NCF_3$ and $CF_3N=NC_2F_5$. The amounts of CF_4 and C_2F_6 formed could account for the two azo compounds that underwent fluorinolysis, all estimated by V.P.C.

Pyrolyses.—The pyrolyzer consisted of a 60'' section of $3/8$ '' copper tubing electrically heated for the middle 48''. 1. At first $(CF_3)_2NF$ (0.024 mole/hr.) was mixed with helium (0.58 mole/hr.) and passed through the pyrolyzer

which had previously been thoroughly purged with helium at the operating temperature (540°). The products were condensed in a glass trap cooled by liquid oxygen, and after 1.25 hr. the product (3.0 cc.) was separated by V.P.C. The major components were CF_4 and $(CF_3)_2N$ with small amounts of CF_3NF_2 , C_2F_6 and unchanged $(CF_3)_2NF$, all identified by infrared. 2. Next $CF_3CF_2NF_2$ (0.02 mole/hr.) and helium (0.52 mole/hr.) were passed through the pyrolyzer at 450°. After 2 hr. the condensed product (4.0 cc.) was separated by V.P.C. The major products as identified by infrared were CF_4 , C_2F_6 , $n-C_4F_{10}$, NF_3 , CF_3NF_2 , $(CF_3)_2NF$ and $(CF_3)_2N$. A small amount of C_3F_8 was also detected. This pyrolysis was repeated several times during which the composition of the product obtained gradually changed until it remained constant as: CF_4 , C_2F_6 , C_3F_8 , $n-C_4F_{10}$, CF_3CN and $(CF_3)_2N$. 3. Finally, $NF_2CF_2CF_2NF_2$ (0.025 mole/hr.) diluted with helium (0.60 mole/hr.) was pyrolyzed at 255°. After 0.5 hr. the condensed product (1.3 cc.) was separated by V.P.C. and identified by infrared as CF_4 , C_2F_6 , $CF_3CF_2NF_2$, CF_3CN , $CF_3N=NCF_3$ and unchanged $NF_2CF_2CF_2NF_2$. At 360°, the products were CF_4 , C_2F_6 , C_3F_8 , $n-C_4F_{10}$, $(CF_3)_2N$, CF_3CN and $CF_3N=CF_2$.

Acknowledgment.—We would like to thank Dr. Wallace S. Brey, University of Florida, for the n.m.r. spectrum of $CF_3NFC_2F_5$, and Dr. John Ruth, Liggett and Myers Research Laboratory, Durham, N. C., for the mass spectra given above.

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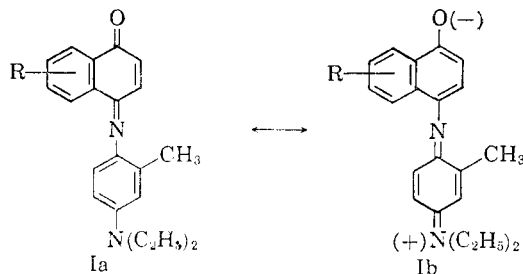
Indoaniline Dyes. V.¹ Some Dyes Derived from Substituted α -Naphthols

BY A. P. LURIE, G. H. BROWN, J. R. THIRTLE AND A. WEISSBERGER

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The synthesis and properties of some substituted α -naphthols and the indoaniline dyes derived from them are reported. Effects of substituents and solvents on the absorption maxima of these dyes, prepared by oxidative condensation of the α -naphthol with 4-amino-3-methyl-N,N-diethylaniline, are explained in terms of electronic and hydrogen-bonding considerations.

An increased contribution of the polarized form (Ib) to the resonance hybrid representing the indo-



aniline dye (I) should cause both a bathochromic shift and an increase in the maximum extinction coefficient. This expectation is based on a study of the indoaniline dyes derived from phenols² and from 1-hydroxy-2-naphthamides.^{1,3} The effect of

substituents in positions other than 2 or 3 on the absorption of indoaniline dyes derived from 1-naphthol is the subject of the present paper.

The data obtained are summarized in Table I. Because an increase in the polarity of the solvent tends to favor the ionic form (Ib) of the dye, the bathochromic and hyperchromic effects observed in proceeding from cyclohexane to butyl acetate to methanol were to be expected.

A plot (Fig. 1) of σ -constants⁴ against $1/\lambda_{max}$ of the dyes derived from 6- and 7-substituted α -naphthols, using *para*-constants and *meta*-constants, respectively, results in straight-line relationships. In these positions, substituents which increase the electron density on the carbonyl oxygen of the dye cause hypsochromic shifts; those which decrease the electron density result in bathochromic shifts. Thus, a methoxy group in position 6, where it can exercise resonance effects, is electron-supplying and gives a hypsochromic shift relative to the dye from α -naphthol; the same group in position 7, owing to its electron-withdrawing inductive effect, causes a bathochromic shift.⁵

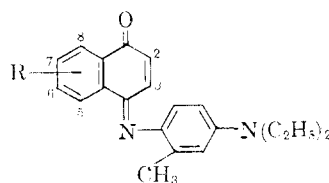
(1) Indoaniline Dyes. IV, C. R. Barr, G. H. Brown, J. R. Thirtle and A. Weissberger, *Phot. Sci. and Eng.*, **5**, 195 (1961).



(2) (a) P. W. Vittum and G. H. Brown, *J. Am. Chem. Soc.*, **68**, 2235 (1946); (b) **69**, 152 (1947); (c) **71**, 2287 (1949).

(3) (a) B. S. Portnaya, I. I. Levkoev and N. S. Spasokukotskil, *Doklady Akad. Nauk SSSR*, **82**, 603 (1952); (b) N. S. Spasokukotskil, I. I. Levkoev and B. S. Portnaya, *ibid.*, **93**, 671 (1953); (c) B. S. Portnaya, N. S. Spasokukotskil, N. F. Turitsyna, T. P. Bobkova, G. I. Arbutov and I. I. Levkoev, *J. Gen. Chem. SSSR*, **28**, 2532 (1956); (d) N. F. Turitsyna, B. S. Portnaya, N. S. Spasokukotskil, T. P. Bobkova, G. I. Arbutov and I. I. Levkoev, *ibid.*, **26**, 2546 (1956).

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188; H. H. Jaffe, *Chem. Revs.*, **63**, 191 (1953); σ^* -values were used when available.

(5) It has been brought to our attention, by one of the referees, that the absorption of substituted indigo and thioindigo dyes (*cf.*

TABLE I
 INDOANILINE^a DYES DERIVED FROM SUBSTITUTED α -NAPHTHOLS


No.	R	M.p., °C.	Crystallized from	λ_{\max} , $m\mu$ ($E_{\max} \times 10^{-4}$) [sharpness] ^b		
				Cyclohexane	<i>n</i> -Butyl acetate	Methanol
1	H	114	Ethanol	582 (1.4) [0.54]	598 (1.6) [0.58]	623 (1.7) [0.62]
2	5-OCH ₃	92	Cyclohexane	588 (1.6) [.64]	602 (1.2) [.65]	620 (1.8) [.76]
3	6-OCH ₃	135	Ethanol	576 (1.3) [.55]	590 (1.5) [.57]	622 (1.6) [.62]
4	7-OCH ₃	153	Ethanol	587 (1.5) [.58]	602 (1.6) [.58]	627 (1.6) [.63]
5	8-OCH ₃	143	Ethanol	570 ° [.55]	584 (1.4) [.59]	622 (1.6) [.64]
6	5-OH	164	Ethanol	589 (1.5) [.67]	600 (1.7) [.60]	624 (1.8) [.63]
7	6-OH	191	Ethanol	576 (1.4) [.55]	585 (1.4) [.61]	617 (1.5) [.65]
8	8-OH	185	Acetone	628 ° [.60]	646 (1.8) [.65]	660 ° [.67]
9	5-NH ₂	152	2-Propanol	574 (1.1) [.68]	592 (1.2) [.69]	624 (1.3) [.72]
10	6-NH ₂	198	Benzene	566 (1.2) [.57]	575 (1.2) [.64]	612 (1.3) [.78]
11	8-NH ₂	120	Ethanol	602 ° [.70]	612 (1.5) [.72]	630 (1.5) [.76]
12	5-NHC ₂ H ₅	108	Ethanol	° ° °	606 (1.3) [.75]	638 (1.4) [.77]
13	5-NHCOCH ₃	198	Ethanol	590 (1.2) [.67]	608 (1.4) [.64]	636 (1.5) [.67]
14	6-NHCOCH ₃	252	Ethanol	580 ° [.60]	590 (1.4) [.59]	627 (1.7) [.65]
15	8-NHCOCH ₃	190	Ethanol	626 (1.9) [.59]	640 (2.0) [.60]	655 (2.1) [.65]
16	5-NHCOC ₃ F ₇ - <i>n</i>	130	Cyclohexane	617 (1.3) [.63]	629 (1.3) [.70]	650 (1.3) [.71]
17	5-NHSO ₂ - 	206	Ethyl acetate	600 (1.8) [.55]	616 (1.9) [.58]	640 (2.0) [.73]
18	8-NHSO ₂ - 	190	Ethanol	629 ° [.58]	646 (2.1) [.59]	663 ° [.61]
19	5-NO ₂	168	Ethanol	613 (2.2) [.46]	623 (2.2) [.52]	646 (2.3) [.61]
20	6-NO ₂	203	Ethyl acetate	618 ° [.50]	636 (2.1) [.57]	658 ° [.64]
21	5-Cl	147	Ethanol	598 ° [.59]	612 (1.4) [.64]	636 (1.5) [.71]
22	7-CH ₃	128	Ethanol	581 (1.4) [.55]	597 (1.5) [.59]	625 (1.6) [.65]
23	6,7-OCH ₃	182	Ethanol	577 (1.3) [.58]	592 (1.5) [.57]	625 (1.6) [.62]
24	5,8-OCH ₃	152	Cyclohexane	554 (0.9) [.60]	566 (1.0) [.62]	600 (1.1) [.72]
25	5,8-OCH ₃ -7-CH ₃	110	Ethanol	556 ° [.60]	570 (0.9) [.66]	596 (0.9) [.73]
26	5,8-Cl	165	Ethanol	587 (1.3) [.57]	600 (1.4) [.61]	620 (1.4) [.71]

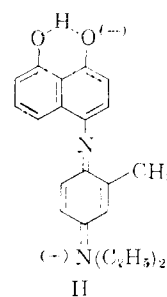
^a For convenience, only the non-polar structure Ia is given. ^b The slope of the spectrophotometric curve in the region of peak absorption is given in terms of sharpness, *s*. For the discussion we have considered only the sharpness on the low wave length side of the absorption curve as given by $s = D_{\lambda_{\max}-40m\mu} / D_{\lambda_{\max}}$. The sharper the curve the smaller will be the *s*-value. ° Too insoluble.

Electron-withdrawing substituents (*e.g.*, nitro-) in position 5 give rise to bathochromic shifts. Methoxy and chloro groups, in this position, also shift the absorption to longer wave lengths in agreement with the fact that they can exert only inductive effects on the absorption of the dye. As can be expected, amido groups in position 5 cause larger bathochromic shifts the greater the inductive effect of the acyl group, as measured by the strength of the corresponding acid. The 5-substituents studied, with the exception of amino, affect the hue of the dye, apparently, by a withdrawal of electrons from the aromatic system as a whole. It is difficult to understand the hypsochromic shift effected by a 5-amino group unless one assumes that a direct interaction between the two N-atoms in the *peri*-positions interferes with the ability of the tertiary nitrogen atom to accept the positive charge.

The similarity in absorptions of the 8-methoxy-, 6-methoxy- and 6-hydroxy-1-naphthol dyes is

J. Formanek, *Z. angew. Chem.*, **41**, 1137 (1928) has been explained in a similar manner by G. M. Wyman and W. R. Brode, *J. Am. Chem. Soc.*, **73**, 1493 (1951).

readily understood in terms of resonance. The observation that the 8-hydroxy-1-naphthol dye absorbs at considerably longer wave lengths can be explained by the hydrogen bonding as shown in II. Such an interpretation is corroborated by the comparison of other 6- and 8-substituents capable of



such hydrogen bonding. An amino group in position 6 causes a hypsochromic shift of 16 $m\mu$ in cyclohexane, relative to that of the unsubstituted 1-naphthol dye, but the same group in position 8 results in a 20- $m\mu$ bathochromic shift. The acet-

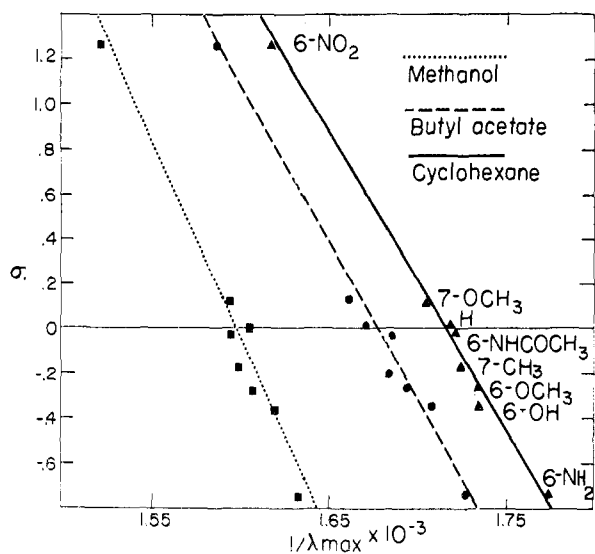


Fig. 1.—Plot of $1/\lambda_{\max}$ (λ_{\max} in $m\mu$) vs. Hammett's σ -constants for indoaniline dyes (I) substituted in the 6- or 7-positions.

amido group in position 6 is without effect but is bathochromic by 44 $m\mu$ in position 8. Analogous chelation effects have been used to explain the difference in absorptions of dyes prepared from 2-acetamido- and 3-acetamidophenol^{2a} and for the differences between dyes from 1-hydroxy-2-naphthamides derived from primary and secondary amines.^{1,3}

The dyes with multiple substitution on the naphthol ring show hypsochromic shifts which are considerably larger than the values calculated by the addition of shifts caused by the individual groups.^{2c} The data seem to indicate that there is a mutual enhancement of electron density toward the aromatic system, particularly in the case of 5,8-dimethoxy substitution.

The data presented indicate that the dominant factor controlling λ_{\max} is the increased or decreased ability of the tertiary nitrogen atom of the *p*-phenylenediamine moiety to accept a positive charge as shown in Ib.

The effect of substituents on extinction and shape of the absorption curve is less readily explained. However, a plot of λ_{\max} vs. E_{\max} (Fig. 2) reveals that where chelation effects between groups in *peri*-positions are not possible, a nearly linear relationship exists. With the exception of 5-hydroxy, -nitro and -*p*-toluenesulfonamido groups, all of the 5-substituted dyes give low extinction coefficients and unsharp absorption curves (see footnote b, Table I). It appears that the absorption becomes broader and the extinction diminishes when additional structures contribute to the resonance hybrid representing the dye.

Experimental⁶

A. Couplers.—Commercially available 1-naphthol, 5-nitro-1-naphthol, 5-*p*-toluenesulfonamido-1-naphthol, 1,5-naphthalenediol and 1,6-naphthalenediol were recrystallized to constant m.p. prior to dye formation.

(6) All melting points are uncorrected. The microanalyses were performed by D. F. Ketchum and associates, Kodak Research Laboratories, Eastman Kodak Co.

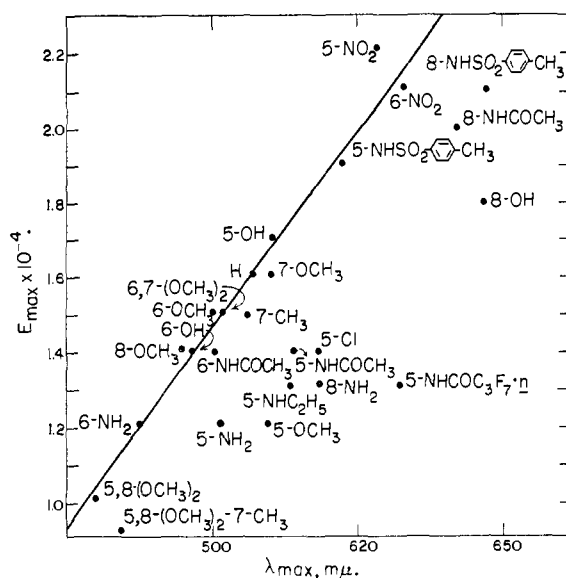


Fig. 2.—Plot of λ_{\max} vs. E_{\max} for α -naphthol indoaniline dyes (I) in butyl acetate.

The following couplers were prepared according to methods described in the literature and gave satisfactory elemental analyses ($\pm 0.3\%$ absolute): 5-methoxy-1-naphthol,^{7a} m.p. 135–136°; 8-methoxy-1-naphthol,^{7b} m.p. 53–54°; 8-amino-1-naphthol,⁸ m.p. 95–96°; 6-acetamido-1-naphthol,⁹ m.p. 95–96°; 8-acetamido-1-naphthol,¹⁰ m.p. 174–175°; 8-*p*-toluenesulfonamido-1-naphthol,¹¹ m.p. 190–192°; 6-nitro-1-naphthol,¹² m.p. 178–180°.

The rest of the couplers are either new compounds or were synthesized by methods superior to those given in the literature. Infrared spectra have been obtained for all couplers and their intermediates; these spectra confirm the structural assignments.

6-Methoxy-1-naphthol.¹³—A mixture of 10 g. (0.058 mole) of 6-methoxy-1-naphthylamine,¹⁴ 40 g. of sodium bisulfite and 100 ml. of water was refluxed 24 hr. and then made alkaline (caution!) with 30% aqueous sodium hydroxide solution and refluxed 24 hr. longer. The filtrate was acidified with 20% aqueous hydrochloric acid and the precipitate recrystallized from ethanol-water to give 6 g. of 6-methoxy-1-naphthol, m.p. 79–80°.

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 75.8; H, 5.8. Found: C, 75.8; H, 6.1.

7-Methoxy-1-naphthol.¹⁵—To a solution of 12 g. (0.06 mole) of 8-acetamido-2-naphthol¹⁶ in 150 ml. of water containing 5.2 g. of sodium hydroxide there was added 13 g. (0.10 mole) of dimethyl sulfate at 25° and the resulting mixture was stirred 4 hr. The precipitate was recrystallized from ethanol-water to give 9.7 g. of 1-acetamido-7-methoxynaphthalene, m.p. 166–167°, lit.¹⁷ m.p. 145°.

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.5; H, 6.1; N, 6.5. Found: C, 72.3; H, 6.2; N, 6.3.

(7) (a) H. E. Fierz-David, L. Blangey and W. von Krannichfeldt, *Helv. Chim. Acta*, **30**, 816 (1947); m.p. 135–136°. (b) H. Staudinger, E. Schlenker and H. Goldstein, *ibid.*, **4**, 334 (1921); m.p. 55–56°.

(8) F. Fichter and R. Gageur, *Ber.*, **39**, 3331 (1906); m.p. 95–97°.

(9) L. Sander, *ibid.*, **58**, 824 (1925); m.p. 100°.

(10) L. C. Raiford and E. P. Clark, *J. Am. Chem. Soc.*, **48**, 483 (1926); m.p. 181°.

(11) F. Fichter and T. Kühnel, *Ber.*, **42**, 4748 (1909); m.p. 189°.

(12) H. H. Hodgson and H. S. Turner, *J. Chem. Soc.*, **8** (1944); m.p. 181–182°.

(13) German Patent 298,098 (1916); no m.p. is given for this compound.

(14) A. Butenandt and G. Schramm, *Ber.*, **68**, 2083 (1935).

(15) Prepared by a rapid distillation of β -anisalpropionic acid, the product has a m.p. significantly different from that reported herein; A. Angeletti, *Gazz. chim. ital.*, **59**, 851 (1929).

(16) F. Kehrman and E. F. Engelke, *Ber.*, **42**, 350 (1909).

(17) W. A. Davis, *Chem. News*, **74**, 302 (1896), has an alternate synthesis.

A solution of 9 g. of potassium hydroxide in 10 ml. of water was added to a solution of 8.4 g. (0.038 mole) of 1-acetamido-7-methoxynaphthalene in 60 ml. of ethanol, refluxed 12 hr. and then poured into 500 ml. of water. The precipitate was recrystallized from methanol-water to give 6 g. of 7-methoxy-1-naphthylamine, m.p. 79.5–80°, lit.¹⁸ m.p. 81°.

Five grams (0.03 mole) of 7-methoxy-1-naphthylamine was converted, as described for the 6-methoxy isomer, to 0.5 g. of 7-methoxy-1-naphthol, m.p. 104.5–105° from ethanol-water; lit.¹⁶ m.p. 122–124°, turning brown at 60°.

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 75.8; H, 5.8. Found: C, 75.8; H, 6.0.

1,8-Naphthalenediol.¹⁹—A mixture of 50 g. of 1-naphthol-8-sulfonic acid (Eastman Kodak Co.), 150 g. of potassium hydroxide, 150 g. of sodium hydroxide and 75 ml. of water was fused slowly, with vigorous stirring, to 230° in a 5-liter stainless-steel beaker. The fusion was interrupted when frothing had ceased and the melt was totally encrusted with black tar. The fluid mixture was poured onto a stainless-steel sheet to effect immediate solidification. The solid mass was crushed and added piecemeal, with vigorous stirring, to 2.5 liters of water containing 700 ml. of concentrated hydrochloric acid and the mixture boiled for 10 min. and filtered hot. The cooled filtrate was extracted with ethyl ether, dried and evaporated. The residue was recrystallized from benzene-ligroin to give 4.3 g. of 1,8-naphthalenediol, m.p. 142–143°, lit.¹⁹ m.p. 140°.

Anal. Calcd. for $C_{10}H_8O_2$: C, 74.9; H, 5.1. Found: C, 75.2; H, 5.3.

5-Amino-1-naphthol.—5-Nitro-1-naphthol (19 g.) in 200 ml. of isopropyl alcohol was reduced in the presence of Raney nickel at 50 p.s.i. hydrogen. The solution of the amine was acidified with concentrated hydrochloric acid, stripped to dryness and the resultant solid converted to the free amine with 5% aqueous sodium carbonate solution. Recrystallization from water gave 12 g. of 5-amino-1-naphthol, m.p. 192–193° dec.; lit. m.p. 170° dec.,^{20a} 192° dec.^{20b}

Anal. Calcd. for $C_{10}H_9NO$: C, 75.4; H, 5.7; N, 8.8. Found: C, 75.2; H, 5.8; N, 8.7.

6-Amino-1-naphthol.—Catalytic hydrogenation under the conditions just given afforded a 95% yield of 6-amino-1-naphthol, m.p. 193–195° dec. (from acetic acid), lit.²¹ m.p. 199.5° dec.

Anal. Calcd. for $C_{10}H_9NO$: C, 75.4; H, 5.7; N, 8.8. Found: C, 75.3; H, 6.0; N, 8.6.

5-Acetamido-1-naphthol.—A mixture of 3.2 g. (0.02 mole) of 5-amino-1-naphthol and 9.8 g. of acetic anhydride was shaken vigorously. During the exothermic reaction, complete solution occurred, followed immediately by solidification. The solid was recrystallized from ethanol-ligroin to give 1.6 g. of 5-acetamido-1-naphthol, m.p. 172–174°.

Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.6; H, 5.5; N, 7.0. Found: C, 71.6; H, 5.8; N, 6.9.

5-Ethylamino-1-naphthol.—Thirty grams (0.15 mole) of 5-acetamido-1-naphthol was converted to 21 g. of 5-acetamido-1-methoxynaphthalene (see 1-acetamido-7-methoxynaphthalene), m.p. 189–190° (from ethanol-ligroin).

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.5; H, 6.1; N, 6.5. Found: C, 72.6; H, 6.3; N, 6.6.

Twenty grains (0.09 mole) of this amide was added to a suspension of 5.7 g. (0.15 mole) of lithium aluminum hydride in 500 ml. of ethyl ether and refluxed 3 days. After decomposition of excess lithium aluminum hydride, the mixture was extracted with 3 liters of ethyl ether which was then decolorized and dried over anhydrous magnesium sulfate. The residue, after evaporation of ethyl ether, was recrystallized from cyclohexane to give 12 g. of 5-ethylamino-1-methoxynaphthalene, m.p. 74.5–75°.

(18) German Patent 477,448 (1926).

(19) H. Erdmann, *Ann.*, **247**, 306 (1888); an alternate method to that reported herein was used.

(20) (a) H. T. Bucherer and A. Uhlmann, *J. prakt. Chem.*, [2] **80**, 20; (1909); (b) N. N. Vorozhtzov and A. A. Kulev, *Bull. inst. polytech. Ivanovo-Voznesensk*, **9**, 87 (1928).

(21) H. T. Bucherer and R. Wahl, *J. prakt. Chem.*, [2] **103**, 129 (1922).

Anal. Calcd. for $C_{13}H_{13}NO$: C, 77.6; H, 7.5; N, 7.0. Found: C, 77.7; H, 7.6; N, 7.2.

A solution of 11 g. (0.06 mole) of 5-ethylamino-1-methoxynaphthalene in 250 ml. of glacial acetic acid containing 125 g. of hydrobromic acid (48%) was refluxed 12 hr. and concentrated to produce an oil. The latter was dissolved in 10% aqueous sodium hydroxide and the alkaline filtrate acidified with 20% aqueous acetic acid, filtered from a small amount of solid, just neutralized with 5% aqueous sodium carbonate and extracted with ethyl ether. After evaporation of the ethyl ether, the residue was recrystallized from benzene to give 5.3 g. of 5-ethylamino-1-naphthol, m.p. 85.5–86°.

Anal. Calcd. for $C_{12}H_{13}NO$: C, 77.0; H, 7.0; N, 7.5. Found: C, 76.8; H, 7.0; N, 7.3.

5-*n*-Heptafluorobutyramido-1-naphthol.²²—To a solution of 3.2 g. (0.02 mole) of 5-amino-1-naphthol and 5.2 g. (0.04 mole) of quinoline in 50 ml. of dioxane there was added at 27°, a solution of 4.7 g. (0.02 mole) of *n*-heptafluorobutyryl chloride (Eastman Kodak Co.) in 20 ml. of dioxane. During the addition, the temperature rose to 42° and an oil separated. The mixture was stirred 1 hr., poured into 300 ml. of water containing 30 ml. of concentrated hydrochloric acid and the precipitate recrystallized from toluene to give 3.7 g. of 5-*n*-heptafluorobutyramido-1-naphthol, m.p. 200–201°.

Anal. Calcd. for $C_{14}H_9F_7NO_2$: C, 47.3; H, 2.2; N, 3.9. Found: C, 47.7; H, 2.4; N, 4.0.

5-Chloro-1-naphthol.²³—Eighty-one grams (0.51 mole) of 5-amino-1-naphthol, suspended in 260 ml. of hydrochloric acid (18%) at –10°, was diazotized with a solution of 38 g. of sodium nitrite in 75 ml. of water in the course of 30 min. The diazonium salt solution was added, in 10 min., to freshly prepared cuprous chloride²⁴ in 800 ml. water containing 250 ml. of concentrated hydrochloric acid at 0°. The mixture was stirred vigorously as it came to room temperature and then heated to 60–70° until no further evolution of gas was detected (measured by downward displacement of water). The cooled mixture was extracted with 5 liters of ethyl ether (46 g. of black solid, presumably an azo dye, remained undissolved), which was then decolorized and evaporated. The residue (10 g., m.p. 117–125°) was recrystallized twice from water and then sublimed at 120° (2 mm.) to give 7 g. of 5-chloro-1-naphthol, m.p. 135.5–136°, lit.²³ m.p. 132°.

Anal. Calcd. for $C_{10}H_7ClO$: C, 67.3; H, 4.0; Cl, 19.9. Found: C, 67.2; H, 4.1; Cl, 19.7.

7-Methyl-1-naphthol.²⁵— β -(4-Methylbenzoyl)-propionic acid²⁶ was prepared in 95% yield by the succinoylation of toluene; only 70% of the amount of toluene suggested²⁶ was used and 2 hr. rather than 15 hr. was allowed for complete reaction (1 hr. for the addition of aluminum chloride at 10°, followed by stirring for 1 hr. at 40°).

To 38 g. (0.2 mole) of this keto-acid and Zn(Hg) (prepared from 110 g. of mossy zinc, 7.8 g. of mercuric chloride and 5.2 ml. of concentrated hydrochloric acid in 120 ml. of water) there was added 115 ml. of concentrated hydrochloric acid in 30 min. and the resultant mixture was refluxed 4 hr. The cooled mixture was extracted with ethyl ether which was dried and concentrated. The residue distilled at 150–154° (1 mm.) to give 28 g. of γ -(4-methylphenyl)-butyric acid, m.p. 58.5–59°, lit.²⁷ m.p. 58–59°.

A mixture of 12 g. (0.07 mole) of 7-methyl-1-tetralone,²⁷ prepared from the compound just described, and 2.5 g. (0.08 mole) of sulfur was heated in a Wood metal-bath for 30 min. at 250–280°. The reaction mixture distilled to give 3.8 g., b.p. 118–121° (0.8 mm.), m.p. 109–110°. Recrystalli-

(22) We are indebted to Mr. C. R. Barr for this synthesis.

(23) This compound has been prepared by a fast distillation of *o*-chlorophenylpropionic acid; H. Erdmann and R. Kirchhoff, *Ann.*, **247**, 366 (1888).

(24) Prepared from 160 g. of $CuSO_4 \cdot 5H_2O$ according to A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1956, p. 600.

(25) Two syntheses are reported for this compound: (a) From 7-methyl-1-naphthylamine, see V. Veselý and J. Kapp, *Rec. trav. chim.*, **44**, 360 (1925). (b) From 2-bromo-7-methyl-1-tetralone, see F. Krollpfeiffer and W. Schäfer, *Ber.*, **56**, 620 (1923).

(26) A. Katzenellenbogen, *ibid.*, **34**, 3828 (1901).

(27) W. Borsche, *ibid.*, **62**, 2077 (1919).

zation from benzene-petroleum ether afforded 3.5 g. of 7-methyl-1-naphthol, m.p. 110.5–111°, lit.²⁸ m.p. 107–108°.

Anal. Calcd. for $C_{11}H_{11}O$: C, 83.5; H, 6.4. Found: 83.8; H, 6.4.

6,7-Dimethoxy-1-naphthol.²⁸—Twenty-eight grams (0.11 mole) of β -(3,4-dimethoxybenzoyl)-propionic acid^{28a} was added to 3 g. of palladium-on-charcoal, suspended in 150 ml. of glacial acetic acid in a Parr bottle, and reduced at 50 p.s.i. hydrogen at 25°. The filtrate was concentrated to 50 ml. and poured into water to give 24 g. of γ -(3,4-dimethoxyphenyl)-butyric acid, m.p. 59–60°, lit.²⁸ m.p. 57–59°. Compared to a 40% yield under Clemmensen conditions,²⁸ the method cited here affords a 95% yield.

Twenty-one grams (0.10 mole) of this γ -butyric acid was covered with 200 g. of anhydrous hydrogen fluoride in a 1-liter copper beaker. The oil obtained, after evaporation of the hydrogen fluoride, was shaken with 250 ml. of water, extracted into ethyl ether, washed with dilute ammonia and dried over anhydrous magnesium sulfate. Upon evaporation of the solvent, there was deposited 15 g. of 6,7-dimethoxy-1-tetralone, m.p. 95–96°, lit.²⁸ m.p. 98–99°. Again this yield is considerably higher than that obtained by Adams^{28a} and Haworth^{28b} who used other conditions to effect cyclization.

The tetralone was then converted to the desired 6,7-dimethoxy-1-naphthol (according to the method cited under 7-methyl-1-naphthol), m.p. 169–171°, lit.²⁸ m.p. 168–169°.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 70.6; H, 5.9. Found: C, 70.7; H, 6.2.

5,8-Dimethoxy-1-naphthol.²⁹—*p*-Dimethoxybenzene was converted to β -(2,5-dimethoxybenzoyl)-propionic acid, m.p. 102.5–103.5 (lit.²⁹ m.p. 103–104°), in 59% yield under the conditions for the 3,4-isomer. This product was reduced with Pd(C), *vide supra*, to give a 92% yield of γ -(2,5-dimethoxyphenyl)-butyric acid, m.p. 64–66° (lit.²⁹ m.p. 65–66°), which was then converted with anhydrous hydrogen fluoride to 5,8-dimethoxy-1-tetralone in 40% yield, m.p. 62–63°, lit.²⁹ m.p. 62°. The conversion to 5,8-dimethoxy-1-naphthol, m.p. 101–102° (lit.²⁹ m.p. 103–104°), in 60% yield, was effected by heating with sulfur at 220 for 30 min.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 70.6; H, 5.9. Found: C, 70.8; H, 5.9.

5,8-Dimethoxy-7-methyl-1-naphthol.³⁰—2,5-Dimethoxytoluene was converted to β -(2,5-dimethoxy-4-methylbenzoyl)-propionic acid, m.p. 177° (lit.³⁰ m.p. 177°), in 90% yield using the conditions cited under 6,7-dimethoxy-naphthol. The keto-acid was reduced to γ -(2,5-dimethoxy-

4-methylphenyl)-butyric acid, m.p. 102° (lit.,³⁰ m.p. 100–101°), in 50% yield under the conditions given for γ -(4-methylphenyl)-butyric acid. Eighty grams (0.33 mole) of this γ -butyric acid was heated on a steam-bath with 160 ml. of sulfuric acid (95%) for 20 min., poured into 1 liter of ice-water and extracted with 4 liters of ethyl ether. The ethereal extract was washed with dil. ammonia, dried and evaporated. The residue was distilled to give 41 g., b.p. 137–140° (0.6 mm.), which crystallized from low-boiling petroleum ether to give 27 g. of 5,8-dimethoxy-7-methyl-1-tetralone, m.p. 39–40°, lit.³⁰ m.p. 38–40°. The tetralone was then converted, by heating with sulfur at 230° for 30 min., to a 40% yield of 5,8-dimethoxy-7-methyl-1-naphthol, m.p. 81.5–82°, lit.³⁰ m.p. 82.5°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 71.5; H, 6.5. Found: C, 71.1; H, 6.5.

5,8-Dichloro-1-naphthol.³¹—Twenty-four grams (0.1 mole) of 5,8-dichloro-1-nitronaphthalene³² was reduced catalytically, at 25°, with Raney nickel in 250 ml. of ethanol at 50 p.s.i. hydrogen. The filtrate was poured into water and the precipitate recrystallized from ethanol-water to give 20 g. of 5,8-dichloro-1-naphthylamine, m.p. 102–103°, lit.³³ m.p. 104°.

A suspension of 25 g. (0.12 mole) of 5,8-dichloro-1-naphthylamine in 100 ml. of water containing 30 ml. of concentrated sulfuric acid at –5° was diazotized with 9.2 g. of sodium nitrite in 39 ml. of water, the temperature being kept below 0°. The diazonium salt solution was added slowly to a vigorously boiling, vigorously stirred mixture of 200 g. of concentrated sulfuric acid, 400 ml. of water and 500 ml. of *o*-dichlorobenzene. When no further evolution of gas was detected, the mixture was cooled and the organic layer was separated and combined with an ethyl ether extract of the aqueous phase. The residue obtained upon removal of dried solvents was distilled to give 2.6 g. of 5,8-dichloro-1-naphthol, b.p. 122–125° (0.6 mm.), m.p. 116–117°, lit.³¹ m.p. 114–115°.

Anal. Calcd. for $C_{10}H_6Cl_2O$: C, 56.4; H, 2.8; Cl, 33.2. Found: C, 56.4; H, 2.9; Cl, 32.9.

B. Preparation of the Dyes.—With the exception of 5-methoxy-1-naphthol, all of the couplers were converted to their indoaniline dyes by the standard method with potassium ferricyanide as the oxidant.¹ A stable dye from 5-methoxy-1-naphthol could be obtained only by using silver chloride as the oxidant.^{2a} All dyes reported gave satisfactory elemental analyses ($\pm 0.3\%$ absolute).

C. Spectrophotometric Measurements.—The dyes were dissolved in Eastman Kodak White Label Grade solvents to give 4×10^{-5} to 8×10^{-5} *M* solutions which were read in 1-cm. cells with the General Electric Automatic Recording Spectrophotometer.

(31) This compound has been prepared from 2,5-dichlorophenyl-paraconic acid: H. Erdmann and E. Schwechten, *Ann.*, **275**, 283 (1893).

(32) German Patent 293,318 (1914).

(33) F. Friedländer, S. Karamessinis and O. Schenk, *Ber.*, **55**, 45 (1922).

(28) (a) R. Adams, T. A. Geissman, B. R. Baker and H. M. Teeter, *J. Am. Chem. Soc.*, **63**, 528 (1941); (b) R. D. Haworth and C. R. Mavin, *J. Chem. Soc.*, 1485 (1932).

(29) This compound is described by M. Asano and J. Hase, *J. Pharm. Soc. Japan*, **63**, 83 (1943). Since a translation of this article was not available, the m.p.'s given for this compound and its intermediates are taken from C. A., **46**, 921 (1952).

(30) See ref. 28; C. A., **46**, 92g (1952).