give 191 mg. of colorless crystals, m.p. 80–83° (lit.[2] m.p. 81–82°). Recrystallization from benzene gave material of m.p. 83–84° (partial melt; clear melt at 190°).

Anal. Calcd. for $C_5H_8O_4$: C, 45.45; H, 6.10; neut. equiv., 66. Found: C, 45.73; H, 6.09; neut. equiv., 72.

Examination of this material by infrared spectroscopy and paper chromatography with 1-propanol–concentrated ammonium hydroxide–water (60:20:20 by volume) as developer indicated that it was mostly glutaric acid (R_f 0.52). No acidic impurities were detected by paper chromatography; the infrared spectra of the oxidation product and glutaric acid were similar, but not superimposable.

The Ferric Chloride Oxidation of 5-Substituted *o*-Semidines and the Polarographic Properties of the Products

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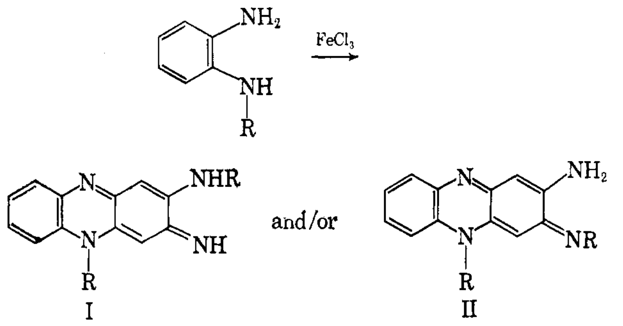
The ferric chloride oxidation of 5-substituted *o*-semidines (2-aminodiphenylamines) yielded 7-substituted 2-amino-3,5-dihydro-5-phenyl-3-phenyliminophenazines as main products, with elimination of one of the 5-substituents of the starting *o*-semidine. Condensation of these phenazine derivatives with ketones led to characteristic Schiff bases. Some polarographic properties of these phenazine derivatives were studied and the effect of substituents on the half-wave potentials was found to be in good agreement with Hammett's σ-values.

The ferric chloride oxidation of mono-*N*-substituted *o*-phenylenediamines has been investigated by Barry *et al.*,[1-3] who have proven that the main oxidation products are phenazine derivatives existing in two isomeric structures I and II which are formed either as a mixture or separately, depending on the nature of the starting amine.

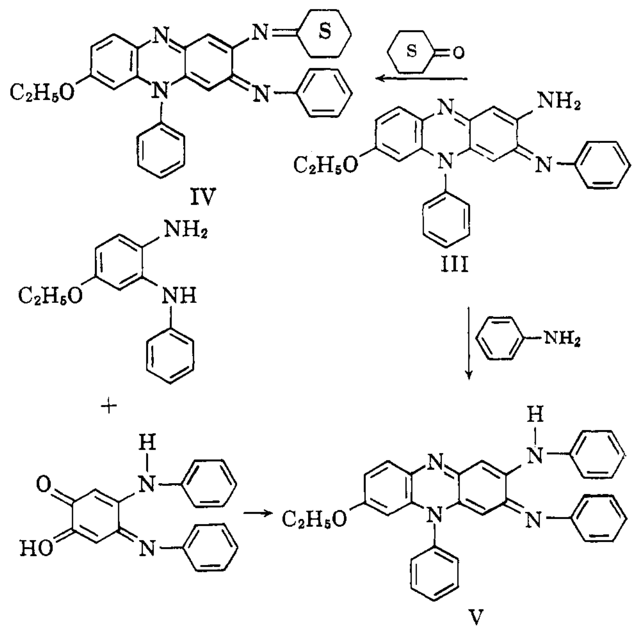


In the oxidation of 2-amino-5-chlorodiphenylamine one chlorine atom is eliminated and only the 7-chloro-II-isomer is formed.

In this laboratory, oxidation products of substituted 2-aminodiphenylamines (*o*-semidines) had been investigated previously as to their suitability as internal indicators in redox titrations. The present paper reports on compounds obtained by the ferric chloride oxidation of some 5-substituted 2-aminodiphenylamines and some of their polarographic properties.

A series of 5-substituted 2-aminodiphenylamines (as the hydrochlorides) were oxidized in aqueous alcoholic solution with ferric chloride. The 5-substituents included various halogen and alkoxy groups. These *o*-semidines were obtained by reduction of the corresponding substituted 2-nitrodiphenylamines, which in turn were prepared by the reaction of substituted anilines with substituted *o*-dinitro- or *o*-halonitrobenzenes. The oxidation products were separated and purified by liquid column chromatography on alumina.

On the basis of the previously cited prior investigations, the deeply colored main oxidation products were expected to be phenazine derivatives with structures analogous to the preceeding I- or II-isomers. This was indeed supported by the elemental analyses of these compounds which also indicated that in each case one of the 5-substituents had been eliminated in the oxidation. Since it seemed not altogether certain whether an alkoxy group would be eliminated in the same fashion as one of the chlorine atoms in the previously mentioned oxidation of 2-amino-5-chlorodiphenylamine, the structure of the main oxidation product of 2-amino-5-ethoxydiphenylamine was determined as 2-amino-3,5-dihydro-7-ethoxy-5-phenyl-3-phenyliminophenazine (III) by the following reactions.



Treatment of this oxidation product with aniline (analogous to Barry, *et al.*,[4]) yields compound V, which was independently synthesized by condensation of 2-amino-5-ethoxydiphenylamine with 4,5-dianilino-*o*-quinone. This proved a structure analogous to either

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[1] V. C. Barry, J. G. Belton, J. F. O'Sullivan, and D. Twomey, *J. Chem. Soc.*, 888 (1956). This paper includes a literature survey of earlier work.

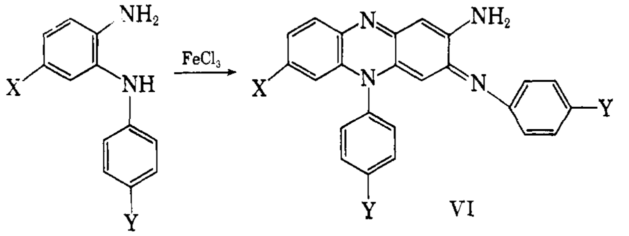
[2] V. C. Barry, J. G. Belton, J. F. O'Sullivan, and D. Twomey, *ibid.*, 893 (1956).

[3] V. C. Barry, J. G. Belton, J. F. O'Sullivan, and D. Twomey, *ibid.*, 896 (1956).

[4] V. C. Barry, J. C. Belton, J. F. O'Sullivan, and D. Twomey, *ibid.*, 895 (1958).

I or II,[4] with the ethoxy group in the 7-position. Structure III (II-isomer) was verified by the condensation of the oxidation product with cyclohexanone to the green Schiff base IV. In a control experiment, a similar green compound was obtained from cyclohexanone and the oxidation product of 2-amino-5-chlorodiphenylamine, for which the structure of a 7-chloro-II-isomer had been ascertained previously.[4]

The formation of green Schiff bases (described in detail later) with cyclohexanone was used subsequently to establish the structure of II-isomers for the oxidation products from other 5-substituted 2-aminodiphenylamines. The newly prepared compounds VI together with the corresponding starting materials are shown.



VI

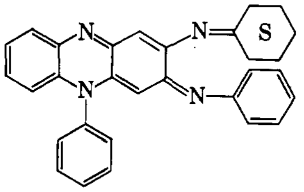
where X = F, Br, I, $-OCH_3$, $-OC_2H_5$ for Y = H
and X = $-OCH_3$ for Y = F, Cl, $-OCH_3$

2-Aminodiphenylamines with a substituent in the 5-position have, it seems, a tendency to form II-isomers on oxidation, provided that the substituent can be eliminated in the reaction. A 5-methyl group would be expected to be very difficult to displace and, in fact, the oxidation product of 2-amino-5-methyldiphenylamine had properties quite different from those of either the I- or II-isomers. The chromatogram of the crude base had a development pattern unlike any of the other investigated compounds. Elution of the orange major band gave a bright red compound which dissolved easily in benzene forming a yellow-orange solution. Three other bands on elution gave yellow-green fluorescent, violet, and blue solutions in benzene. The structure of the major constituent has yet not been determined. Similar observations were reported[5] for the oxidation of 2-amino-4-methyldiphenylamine where the stable methyl group in the 4-position also prevents the formation of the phenazine skeleton which involves both the 4- and 5-positions of the starting amine.

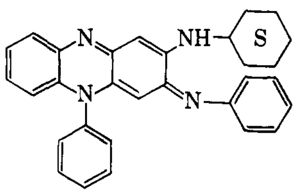
On the other hand, the lack of a substituent in the 5-position of the starting amine causes the formation on oxidation of either a mixture of both isomers or the I-isomer exclusively, as has been shown by Barry, *et al.*[1,3]

Schiff Bases from II-Isomers by Condensation with Cyclohexanone.—As previously mentioned, the reaction of the II-isomers with cyclohexanone in acid solutions resulted in the formation of green compounds which were distinctly different from the glyoxalino derivatives obtained by Barry, *et al.*,[1,6] in reactions of I-isomers with ketones. These glyoxalines were described as yellow to orange-red compounds which were quite soluble, exhibited a greenish yellow fluorescence in solution, and when chromatographed on alumina formed a rather fast moving band on elution with benzene.

From the experimental results, it appears quite clear that these green compounds are Schiff bases of type VII. The new carbon–nitrogen double bond of the cyclohexylideneamino group can then be responsible for the color difference between the Schiff bases and the parent II-isomers by extending the resonance system of the phenazine skeleton. The color change of the Schiff bases from green to red in hydroxylic solvents (especially rapid in the presence of traces of acid) suggests a protonation of the cyclohexylideneamino double bond, thus interrupting the conjugation with the phenazine system and possibly initiating the addition of water (or alcohol) to form amino-hydroxyl (or amino-alkoxy) ketals.



VII



VIII

Further substantiation of the structure of these green compounds as Schiff bases was obtained from hydrogenation experiments on the Schiff base of 2-amino-3,5-dihydro-7-ethoxy-5-phenyl-3-phenyliminophenazine. The chromatographic behavior of this substance was very similar to that of compound IV. The infrared spectrum of this new compound had a single band in the N–H region, thus suggesting the presence of a secondary amine. Both elementary analysis and infrared spectrum indicated that the cyclohexyl group had been preserved in the molecule. Similar results also were obtained for the methoxy analog.

From the foregoing evidence, it appears that during the reduction of the Schiff base VII both the quinoidal system and the carbon–nitrogen double bond of the cyclohexylideneamino group are hydrogenated and in the reoxidation only the quinoidal system is reformed. The structure of the new compound can then be represented correctly by formula VIII.

Thus the formation of the Schiff base, its reduction and reoxidation leads in effect to an alkylation of the free amino group of the original II-isomer. The nature of the *N*-substituent thus introduced will, obviously, depend on the structure of the carbonyl compound employed in the formation of the Schiff base.

Some Polarographic Properties of These Phenazine Derivatives.—The substituted 2-amino-3-anilino-5-phenylphenazinium chlorides described earlier are compounds which, *in alcoholic solutions*, are *intensely* red. This property suggested their possible use as internal redox indicators. Preliminary studies have indicated the feasibility of these compounds in the titration of dissolved oxygen with chromium(II) and europium(II) solutions. In these cases, the phenazine is reduced rapidly to a greenish yellow solution of the semiquinone in acid solution.. The reduction product in turn is readily reoxidized by oxygen to the colored phenazine. However, their surprisingly low solubility in water and aqueous alcoholic solutions compared to other 5-phenylphenazinium compounds, such as the commercial safranines and phenosafranine, discouraged such use.

However, it still remained possible to determine the effect of a substituent group in terms of the difference

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(5) V. C. Barry, J. G. Belton, M. L. Conalty, and D. Twomey, *Nature* **162**, 622 (1948).

(6) V. C. Barry, J. G. Belton, J. F. O'Sullivan, and D. Twomey, *J. Chem. Soc.*, 3347 (1956).

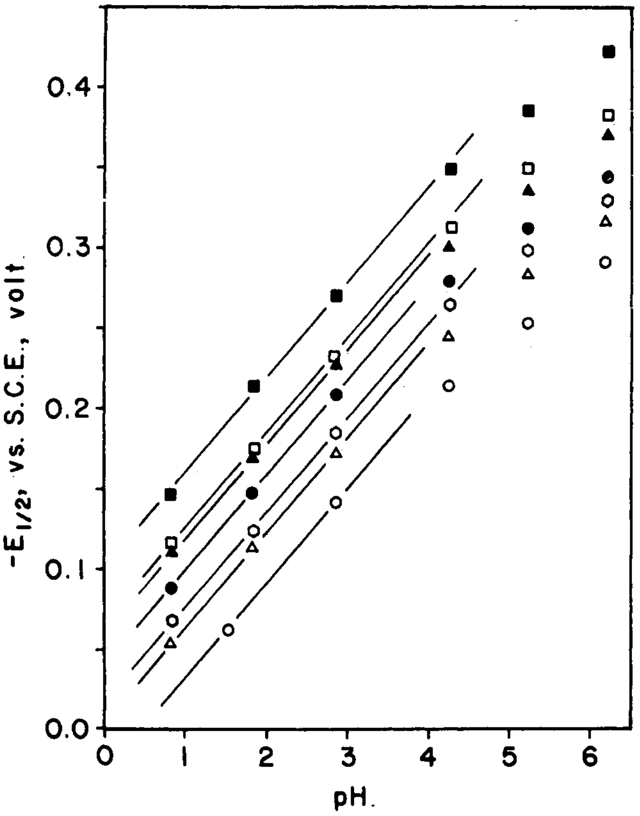
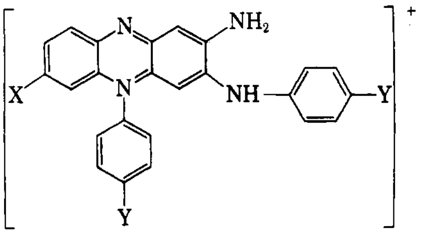


Fig. 1.—Half-wave potential–pH dependence of substituted 2-amino-3-anilino-5-phenylphenazinium chlorides: ■ X = Y = $-OCH_3$; □ X = $-OCH_3$, Y = H; ▲ X = $-OCH_3$, Y = F; ● X = $-OCH_3$, Y = Cl; ⬡ X = Y = H; △ X = F, Y = H; and ○ X = Br, Y = H.

in the reduction potential between the substituted and unsubstituted compounds. Polarographic techniques provided a means for such an investigation.

As representative compounds for study, those that had the structure that follows were considered, where



X = H, F, and Br for Y = H; X = $—OCH_3$ for Y = H, F, Cl, and $—OCH_3$. The choices were guided somewhat by Hammett's σ-values for *para* substitution. The polarographic data reported here were obtained at a concentration of 0.25 m*F* in 3:1 95% ethanol–water solutions with lithium acetate–nitric acid buffers and with lithium nitrate added to increase the ionic strength to 0.25 *M*. The choices for solvent composition and supporting electrolyte were governed by solubility considerations.

In experiments to determine the effects of concentration, solutions 0.50 and 0.75 m*F* gave waves similar to those obtained with the 0.25 m*F* solution. Likewise, half-wave potentials obtained over the ionic strength range of 0.05 to 0.25 *M* were the same after corrections were applied for changes in pH and *iR* drop.

It was found advisable to prepare the ethanolic solutions just prior to the polarographic runs. A small prewave was observed with some of the solutions that had been allowed to stand for one or two days. These waves were $^1/_{20}$–$^1/_{25}$ the height of the main wave and occurred at a potential about 0.2 volt more positive. Among the solutions that were set aside for one to two months, that of the bromo (X = Br, Y = H) compound did not develop such a wave while the prewave of the fluoro (X = F, Y = H) compound increased slightly. The analogous waves of the methoxy (X = $—OCH_3$, Y = H) and methoxyfluoro (X = $—OCH_3$, Y = F) phenazinium chlorides in a month's period had increased to about a third of the height of the original main wave. In all cases, the total height of the two waves remained about constant. The cause of the anomalous waves has not been established.

The experimental half-wave potentials are summarized in Table I. The pH values are "apparent" ones obtained with a glass electrode. The estimated precision for the pH measurements and the half-wave potentials are ±0.02 pH units and ±2 mv., respectively.

TABLE I

MEASURED HALF-WAVE POTENTIALS (S.C.E.) AT VARIOUS pH VALUES

A. Dimethoxy (X = Y = $—OCH_3$)						
pH	0.85	1.88	2.88	4.28	5.26	6.24
$-E_{1/2}$, v.	0.147	0.214	0.271	0.349	0.386	0.423
B. Methoxy (X = $—OCH_3$, Y = H)						
pH	0.86	1.88	2.85	4.29	5.25	6.23
$-E_{1/2}$, v.	0.117	0.175	0.233	0.313	0.350	0.383
C. Methoxyfluoro (X = $—OCH_3$, Y = F)						
pH	0.86	1.86	2.88	4.26	5.25	6.23
$-E_{1/2}$, v.	0.111	0.170	0.228	0.301	0.336	0.371
D. Methoxychloro (X = $—OCH_3$, Y = Cl)						
pH	0.85	1.86	2.88	4.27	5.26	6.23
$-E_{1/2}$, v.	0.089	0.148	0.209	0.280	0.313	0.345
E. Unsubstituted (X = Y = H)						
pH	0.87	1.87	2.88	4.28	5.26	6.23
$-E_{1/2}$, v.	0.068	0.124	0.185	0.265	0.298	0.330
F. Fluoro (X = F, Y = H)						
pH	0.85	1.86	2.88	4.26	5.25	6.20
$-E_{1/2}$, v.	0.054	0.114	0.173	0.245	0.284	0.317
G. Bromo (X = Br, Y = H)						
pH		1.57	2.88	4.27	5.25	6.20
$-E_{1/2}$, v.		0.065	0.142	0.215	0.254	0.292

The tabular data is presented graphically in Fig. 1. The $-E_{1/2}$ *vs.* pH slope, for all compounds, in the low pH region is, within experimental error, 0.059 volt/pH unit, and at higher pH values decreases, approaching 0.030 volt/pH unit.

In Table II, the substituent effects in terms of the half-wave potentials are summarized as differences, $\Delta E_{1/2}$, between a substituted compound and the selected reference compound. $(\Delta E_{1/2})_1$ represents the compounds with Y = H and X = substituent with the unsubstituted compound (X = Y = H) as the reference and $(\Delta E_{1/2})_2$ represents those with X = $-OCH_3$ and Y = substituent with the methoxy (X = $-OCH_3$, Y = H) compound as the reference. The $\Delta E_{1/2}$ values are the average differences in the region where the $-E_{1/2}$ *vs.* pH slope is 0.059 volt/pH unit. The shifts in the half-wave potentials are in the direction expected if one considers the electron donating and withdrawing tendencies of the substituents. Good correlation with the Hammett σ-values for *para* substitution[7] is shown in Fig. 2.

Table II

Changes in the Half-Wave Potential Resulting from Substituent Effects

Compound	$(\Delta E_{1/2})_1$	$(\Delta E_{1/2})_2$
Dimethoxy ($X = Y = -OCH_3$)	. . .	−0.035
Methoxy ($X = -OCH_3$, $Y = H$)	−0.050	0.000
Methoxyfluoro ($X = -OCH_3$, $Y = F$)	. . .	0.006
Methoxychloro ($X = -OCH_3$, $Y = Cl$)	. . .	0.027
Unsubstituted ($X = Y = H$)	0.000	. . .
Fluoro ($X = F$, $Y = H$)	0.011	. . .
Bromo ($X = Br$, $Y = H$)	0.043	. . .

In order to determine the reversibility of the waves and the mechanism of the electroreduction of the phenazinium chlorides, a preliminary hydrogenation experiment was performed. A plot of $-E_{\text{d.m.e.}}$ *vs.* $\log i/(i_d - i)$ had indicated a one-electron reduction in the low pH region and a two-electron reduction at higher pH values. This was consistent with pH data in Fig. 1 since a one-electron reduction to a semiquinone would require one proton. Hydrogenation of a sample at low pH with palladium-on-charcoal catalyst gave a deep green solution typical of those of semiquinones. Similar treatment of a solution at higher pH values resulted in a yellow-green solution. A polarogram of a low pH solution partially hydrogenated had a composite anodic–cathodic wave with no inflection in the vicinity of the residual current, hence, indicating reversibility between the semiquinone and the phenazine. Further investigations are currently being undertaken to determine electron spin resonance and chronopotentiometric characteristics and the effect of other X- and Y-substituent combinations on Fig. 2 type plots.

Experimental

The Ferric Chloride Oxidation of 5-Substituted *o*-Semidines. I. Synthesis of Substituted 2-Nitrodiphenylamines. Starting Materials.—Aniline and *p*-anisidine were redistilled under reduced pressure from a small amount of zinc dust. *p*-Chloroaniline was used without further purification. All were Eastman White Label. *p*-Fluoroaniline was prepared by tin–hydrochloric acid reduction of *p*-fluoronitrobenzene, obtained by thermal decomposition of the tetrafluoroborate diazonium salt of *p*-nitroaniline.[8]

3,4-Dinitrohalobenzenes were prepared by nitration of the appropriate 1-halo-3-nitrobenzene with a mixture of sulfuric and fuming nitric acids. The chloro compound was purified by reduced pressure distillation, b.p. 115 (0.3), 120 (0.6), and 127° (1 mm).[9] The bromo, m.p. 58.0–58.5° (lit.[10] 59.4, 59–59.5°), and iodo, m.p. 73–74° (lit.[11] 74°), were recrystallized from 95% ethanol.

2,4-Difluoronitrobenzene was prepared according to Finger and Kruse.[12] 3,4-Dinitrotoluene was obtained through a two-step oxidation of 4-amino-3-nitrotoluene with Caro's acid[13] and fuming nitric acid[14] followed by reduced pressure molecular distillation and recrystallization from methanol, m.p. 58.3–59.0°.

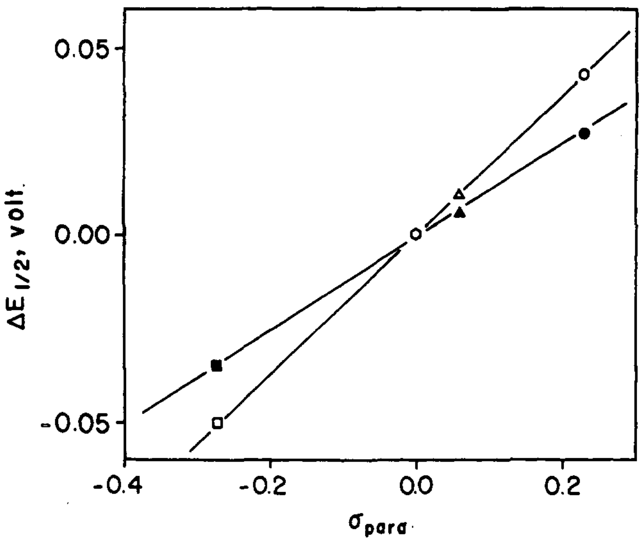


Fig. 2.—Plot of $\Delta E_{1/2}$ values of Table II *vs.* substituent constants, σ_{para}. Legend: same as in Fig. 1.

2-Nitrodiphenylamine (Eastman Kodak 3906) was recrystallized from 95% ethanol.

5-Chloro-2-nitrodiphenylamine.—A solution of 102 g. (0.5 mole) of 1-chloro-3,4-dinitrobenzene and 140 ml. (1.5 moles) of aniline in 500 ml. of 95% ethanol was allowed to stand for 72 hr. The product was filtered, washed with cold ethanol until free of dark discolorations, digested with 3 *N* hydrochloric acid, and recrystallized from ethanol. Yield was 81 g. (65%), m.p. 112.2–112.6° (cor.) (lit.[15] 108.5°, from 2,4-dichloronitrobenzene, 110°[16]).

5-Bromo-2-nitrodiphenylamine.—1-Bromo-3,4-dinitrobenzene (125 g., 0.5 mole) treated as the preceding chloro analog gave 85 g. (57%) of product, m.p. 117.9–118.9° (cor.) (lit.[17] 116°).

5-Iodo-2-nitrodiphenylamine.—3,4-Dinitroiodobenzene (50 g., 0.17 mole) treated as the previous chloro analog gave 21 g. (36%) of product, m.p. 113.5–114.0° (lit.[18] 111°).

5-Chloro-4′-methoxy-2-nitrodiphenylamine.—One hundred grams (0.5 mole) of 1-chloro-3,4-dinitrobenzene treated with *p*-anisidine by the procedure given in the previous section for 5-chloro-2-nitrodiphenylamine, gave on recrystallization from 95% ethanol, 86 g. (62%) of product, m.p. 115.9–116.4°. The analytical sample on further recrystallization from petroleum ether (J. T. Baker, b.p. 20–40°) gave m.p. 115.7–116.2°.

Anal. Calcd. for $C_{13}H_{11}O_3N_2Cl$: C, 56.02; H, 3.98; N, 10.05. Found: C, 56.23; H, 3.89; N, 10.06.

4′,5-Dichloro-2-nitrodiphenylamine.—A solution of 20.3 g. (0.1 mole) of 1-chloro-3,4-dinitrobenzene and 41.5 g. (0.3 mole) of *p*-chloroaniline in 150 ml. of 95% ethanol was heated at 40–50° for 4 hr. The crystalline product obtained upon cooling was filtered, washed with cold ethanol, digested with 3 *N* hydrochloric acid, and recrystallized from ethanol. Yield was 15 g. (53%), m.p. 158.0–158.5° (lit.[16] from 2,4-dichloronitrobenzene, 156°).

5-Fluoro-2-nitrodiphenylamine.[19]—In a modification of the Suschitzky procedure, a solution containing 17 g. (0.11 mole) of 2,4-difluoronitrobenzene and 30 ml. (0.33 mole) of aniline in 100 ml. of 95% ethanol was allowed to stand for 48 hr. Refluxing was prevented by the precipitation of insoluble plates, later identified as aniline hydrofluoride, $C_6H_5NH_2.4HF$, by infrared spectrophotometric comparison with an authentic sample.[20] The mixture of crystals obtained upon cooling was isolated and extracted with ethyl ether. The ether was removed and the de-

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(7) *E.g.*, H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(8) A. Roe, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 193.

(9) For preparations involving recrystallization, see, *e.g.*, A. Laubenheimer, *Ber.*, **9**, 760 (1876).

(10) W. Korner, *Gazz. chim. ital.*, **4**, 349 (1874); A. Mangini, *ibid.*, **66**, 675 (1936).

(11) R. S. Kapil, *J. Chem. Soc.*, 4127 (1959).

(12) G. C. Finger and C. W. Kruse, *J. Am. Chem. Soc.*, **78**, 6034 (1956).

(13) W. D. Langley, "Organic Syntheses." Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 334.

(14) J. Meisenheimer and E. Hess, *Ber.*, **52**, 1161 (1919).

(15) A. Laubenheimer, *ibid.*, **9**, 760 (1876).

(16) V. F. Borodkin, *Zh. Prikl. Khim.*, **21**, 987 (1948).

(17) P. Jacobson and R. Grosse, *Ann.*, **303**, 323 (1898).

(18) P. Jacobson, F. K. Fertsch, and F. Heubach, *ibid.*, **303**, 330 (1898).

(19) H. Suschitzky, *J. Chem. Soc.*, 3042 (1953).

(20) J. F. T. Berliner and R. M. Hann, *J. Phys. Chem.*, **32**, 1142 (1928).

sired product was recrystallized from 95% ethanol. Yield was 18 g. (73%), m.p. 92.0–93.5° (lit.[19] 93–94°).

5-Chloro-4'-fluoro-2-nitrodiphenylamine.—A mixture of 26 g. (0.23 mole) of *p*-fluoroaniline, 47 g. (0.23 mole) of 1-chloro-3,4-dinitrobenzene, and 33 g. (0.4 mole) of sodium acetate in 250 ml. of 95% ethanol was refluxed on a steam bath for 12 hr. Upon cooling, the solid was isolated, washed with cold ethanol, water, and 10% sodium bicarbonate solution, digested with 3 *N* hydrochloric acid, and recrystallized twice from ethanol. Yield was 15 g. (25%), m.p. 110.0–110.6°.

Anal. Calcd. for $C_{12}H_8N_2O_2ClF$: C, 54.05; H, 3.02; N, 10.51. Found: C, 54.22; H, 3.31; N, 10.76.

5-Methoxy-2-nitrodiphenylamine.—To 25 g. (0.085 mole) of 5-bromo-2-nitrodiphenylamine was added a solution prepared by dissolving 5 g. (0.22 mole) of sodium in 375 ml. of absolute methanol. The resulting solution was refluxed for 48 hr. Upon cooling, the crystalline product was isolated, washed with water, and recrystallized from 95% ethanol. Yield was 18.5 g. (89%), m.p. 112.5–113.2°. The analytical sample on further recrystallization had m.p. 112.6–113.3°.

Anal. Calcd. for $C_{13}H_{12}N_2O_3$: C, 63.92; H, 4.95; N, 11.47. Found: C, 63.81; H, 5.20; N, 11.25.

4'-Fluoro-5-methoxy-2-nitrodiphenylamine.—5-Chloro-4'-fluoro-2-nitrodiphenylamine (6 g., 0.023 mole) was treated with sodium methoxide solution (5 g. of sodium in 250 ml. of methanol) as before. Upon two recrystallizations from methanol, the yield was 5 g. (87%), m.p. 112.2–112.7°.

Anal. Calcd. for $C_{13}H_{11}N_2O_3F$: C, 59.54; H, 4.23; N, 10.68. Found: C, 59.84; H, 4.31; N, 10.77.

4'-Chloro-5-methoxy-2-nitrodiphenylamine.—4',5-Dichloro-2-nitrodiphenylamine (5.7 g., 0.02 mole) was treated with sodium methoxide solution (9 g. of sodium in 800 ml. of methanol) as before. Upon recrystallization from methanol, the yield was 4.8 g. (86%), m.p. 131.4–131.9°.

Anal. Calcd. for $C_{13}H_{11}N_2O_3Cl$: C, 56.02; H, 3.98; N, 10.05. Found: C, 56.25; H, 4.19; N, 9.86.

4',5-Dimethoxy-2-nitrodiphenylamine.—5-Chloro-4'-methoxy-2-nitrodiphenylamine (40 g., 0.144 mole) was treated with sodium methoxide solution (10 g. of sodium in 750 ml. of methanol) as before. Recrystallization from 95% ethanol gave 38 g. (97%) of product, m.p. 105.6–106.2°. The analytical sample on further recrystallization from ethanol had m.p. 106.0–106.5°.

Anal. Calcd. for $C_{14}H_{14}O_4N_2$: C, 61.30; H, 5.15; N, 10.21. Found: C, 61.17; H, 5.21; N, 10.29.

5-Ethoxy-2-nitrodiphenylamine.—To 29 g. (0.117 mole) of 5-chloro-2-nitrodiphenylamine in a pressure bottle was added a solution prepared by dissolving 6 g. (0.26 mole) of sodium in 400 ml. of commercial absolute ethanol. The bottle was sealed and heated at 100° for 48 hr. Upon cooling, the crystalline product was isolated, washed with 3 *N* hydrochloric acid, and recrystallized from 95% ethanol with the aid of charcoal. Yield was 24 g. (71%), m.p. 107.5–108.0° (lit.[21] 106–106.5°).

5-Methyl-2-nitrodiphenylamine.—Ten grams (0.055 mole) of 3,4-dinitrotoluene, 15 ml. (0.16 mole) of aniline, and 5 g. of sodium acetate in 50 ml. of nitrobenzene was heated 48 hr. at 150°. The nitrobenzene was removed by steam distillation and the residue extracted with ethyl ether. The product, obtained by drying the extract and evaporating the solvent, was placed on alumina (Merck 71707) with benzene and eluted with *n*-pentane. Upon recrystallization from light petroleum (Skelly B), the yield was 7 g. (56%), m.p. 109–110°. The analytical sample on further recrystallization had m.p. 111.2–111.6°.

Anal. Calcd. for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.72; H, 5.08; N, 12.23.

The structure was confirmed by infrared spectrophotometric comparison with an authentic sample obtained by desulfonation of barium 4-anilino-2-methyl-5-nitrobenzenesulfonate, m.p. 110°.[22]

II. Synthesis of Substituted 2-Amino-3,5-dihydro-5-phenyl-3-phenyliminophenazines. General.—The 2-nitrodiphenylamines were reduced to the amine by hydrogenation in 95% ethanol with 0.5 g. of 10% palladium-on-charcoal (Matheson Coleman and Bell 5865) as catalyst unless otherwise stated.

Melting point determinations (uncorrected) were made on a Kofler micro hot stage (A. H. Thomas Co.) and the reported decomposition points are temperatures at which the crystals appeared to deform. The compounds discolored when heated above 200°.

The alumina used in the chromatographic purifications were Merck chromatographic grade 71707, Woelm basic (Brockmann) activity grade I, and Harshaw 90% catalyst 0101P. The Harshaw product was neutralized with ethyl acetate, washed with water and methanol, dried, and activated by heating for several days at 150°. The hydrochlorides of the substituted phenazines were prepared by treating a solution of the compound in methanol with a slight excess of hydrochloric acid. The salt thus obtained was recrystallized twice from methanol.

All these compounds have rather low solubility in alcohols, are moderately soluble in benzene, dichloromethane and acetic acid, and are very sparingly soluble in ether, and insoluble in water and carbon tetrachloride. All 7-alkoxylated bases form crystals with a green luster while the 7-halogenated ones are brown. The hydrochlorides of these compounds are needles or plates with golden green luster and dissolve in alcohols to give violet-red solutions, while the solutions of the free bases in organic solvents are red-brown.

The microanalyses were performed by Dr. Adalbert Elek and Miss Heather King.

2-Amino-3,5-dihydro-7-ethoxy-5-phenyl-3-phenyliminophenazine.—Three grams of 2-amino-5-ethoxydiphenylamine hydrochloride, obtained by hydrogenation of 5-ethoxy-2-nitrodiphenylamine in 95% ethanol and subsequent precipitation in anhydrous ethyl ether with gaseous hydrogen chloride, was dissolved in 220 ml. of 3:1 95% ethanol–water and oxidized with a solution containing 7 g. of ferric chloride hexahydrate in 70 ml. of water. After stirring for 3.5 hr., the crude hydrochloride was isolated, dissolved in methanol, and precipitated as the free base with ammonium hydroxide. The 2.25 g. of base thus obtained was chromatographed on alumina (450 g. of Woelm activity III) with benzene. The major red band gave, on elution and recrystallization from benzene 1.78 g. (77%) of crystals with a greenish luster, dec. pt. 245–248°.

Anal. Calcd. for $C_{26}H_{22}N_4O$: C, 76.82; H, 5.46; N, 13.78; C_2H_5O, 11.09. Found: C, 76.58; H, 5.36; N, 13.57; C_2H_5O, 10.83.

The hydrochloride was obtained as needles with a golden green luster.

Anal. Calcd. for $C_{26}H_{22}N_4O \cdot HCl$: C, 70.50; H, 5.23. Found: C, 70.31; H, 5.32.

Material from a second red band, much slower moving and narrow, was obtained by extrusion and treatment of the adsorbent with benzene–methanol. This material (after removal of solvent) was rechromatographed with benzene on alumina (Woelm activity IV). Similarly to the original chromatogram, two bands were observed, a broad red band and a slow narrow one. Elution and recrystallization of the first band gave 0.15 g. of material which was identical with the earlier product when compared by decomposition point and infrared spectrophotometry (potassium bromide pellet).

This behavior suggests the presence of an equilibrium between two isomeric structures of the same compound, one being more strongly absorbed than the other, causing the observed separation of bands on the column. In solution, however, the equilibrium seems to be re-established rapidly, thus preventing ready isolation of the pure isomers. These results were obtained regardless of whether or not the solutions, prior to chromatography, were heated to the boiling point of benzene or maintained at room temperature. Similar behavior was observed with the methoxy and the dimethoxy ($X = Y = -OCH_3$) analogs.

2-Anilino-3,5-dihydro-7-ethoxy-5-phenyl-3-phenyliminophenazine.—(A) A mixture of 0.37 g. of 2-amino-3,5-dihydro-7-ethoxy-5-phenyl-3-phenyliminophenazine hydrochloride, 0.11 g. of aniline hydrochloride, and 6 ml. of aniline was refluxed for 12 min. The crude product, obtained by pouring the cooled reaction mixture into ethyl ether, was isolated, dissolved in methanol, and precipitated as the free base with ammonium hydroxide. The base was chromatographed on alumina (Woelm activity III) with benzene. Two strong bands developed, the faster being the desired product and the other larger band the unchanged starting material. The product, when rechromatographed on activity II alumina and recrystallized from benzene–methanol, resulted in 0.068 g. (17%) of brown crystals.

(B) A solution of 1.6 g. of 2-amino-5-ethoxydiphenylamine hydrochloride and 1.8 g. of 4,5-dianilino-*o*-quinone (from the oxidative condensation of catechol and aniline with potassium

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[21] P. Jacobson, F. C. Fertsch, and W. Fischer, *Ber.*, **26**, 681 (1893).

[22] C. Schraube and E. Romig, *ibid.*, **26**, 575 (1893).

iodate,[23] m.p. 193°) in 100 ml. of 95% ethanol was refluxed for 2 hr. Upon cooling, the product was isolated, recrystallized from 95% ethanol, converted to the free base with ammonium hydroxide, and chromatographed on alumina (Woelm activity III) with benzene. The product obtained from elution of the rapid major band was recrystallized from benzene. Yield was 1.6 g. (55%) of brown crystals, dec. pt. 252–254°.

Anal. Calcd. for $C_{32}H_{26}N_4O$: C, 79.28; H, 5.43; N, 11.61; C_2H_5O, 9.34. Found: C, 79.16; H, 5.29; N, 11.40; C_2H_5O, 9.30.

The hydrochloride was obtained as needles with greenish luster.

Anal. Calcd. for $C_{32}H_{26}N_4O \cdot HCl$: C, 74.05; H, 5.24. Found: C, 74.16; H, 5.33.

The decomposition points and infrared spectra (potassium bromide pellets) of both preparations were identical.

2-Amino-3,5-dihydro-7-methoxy-5-phenyl-3-phenyliminophenazine.—To the solution obtained by hydrogenating 3 g. of 5-methoxy-2-nitrodiphenylamine in 120 ml. of 95% ethanol was added 2 ml. of hydrochloric acid and then an oxidizing solution containing 8 g. of ferric chloride hexahydrate in 80 ml. of water. After stirring for 2 hr., the mixture was diluted with water and crude hydrochloride, which crystallized, was isolated, dissolved in methanol, and precipitated as the free base with ammonium hydroxide. The base, 1.7 g., was chromatographed on alumina (500 g. of Merck with 8 wt. % of water added) with benzene as solvent and 95:1 benzene–ether as eluent. Elution of the major band, removal of solvent and recrystallization from benzene gave 1.52 g. (62%) of crystals with a greenish luster, dec. pt. 252–254°.

Anal. Calcd. for $C_{25}H_{20}N_4O$: C, 76.51; H, 5.14; N, 14.28; CH_3O, 7.91. Found: C, 76.58; H, 5.14; N, 14.30; CH_3O, 7.81.

The hydrochloride was obtained as needles with greenish luster.

Anal. Calcd. for $C_{24}H_{20}N_4O \cdot HCl$: C, 70.00; H, 4.93. Found: C, 69.98; H, 5.36.

2-Amino-5-*p*-anisyl-3-*p*-anisylimino-3,5-dihydro-7-methoxyphenazine was obtained in 72% yield from 4′,5-dimethoxy-2-nitrodiphenylamine by the above procedure as crystals with greenish luster, dec. pt. 258–260°.

Anal. Calcd. for $C_{27}H_{24}N_4O_3$: C, 71.66; H, 5.34; CH_3O, 20.58. Found: C, 71.65; H, 5.21; CH_3O, 20.51.

The hydrochloride was obtained as needles with greenish luster.

Anal. Calcd. for $C_{27}H_{24}N_4O_3 \cdot HCl \cdot H_2O$: C, 63.96; H, 5.38; Cl, 6.99. Found: C, 64.24; H, 5.24; Cl, 7.07.

2-Amino-3,5-dihydro-5-*p*-fluorophenyl-3-*p*-fluorophenylimino-7-methoxyphenazine was obtained in 77% yield from 4′-fluoro-5-methoxy-2-nitrodiphenylamine by the above procedure as crystals with greenish luster, dec. pt. 244–246°.

Anal. Calcd. for $C_{25}H_{18}N_4OF_2$: C, 70.08; H, 4.23; CH_3O, 7.24. Found: C, 70.17; H, 4.37; CH_3O, 7.31.

The hydrochloride was obtained as needles with a golden green luster.

Anal. Calcd. for $C_{25}H_{18}N_4OF_2 \cdot HCl$: C, 64.59; H, 4.12. Found: C, 64.30; H, 4.42.

2-Amino-5-*p*-chlorophenyl-3,5-dihydro-3-*p*-chlorophenylimino-7-methoxyphenazine.—A solution of 4 g. of 4′-chloro-5-methoxy-2-nitrodiphenylamine, 12 g. of iron filings, and 4 ml. of acetic acid in 220 ml. of 50% ethanol was refluxed for 1.5 hr. and extracted with ethyl ether. The ethereal phase was dried with sodium hydroxide and the hydrochloride of the product precipitated with hydrogen chloride gas. The amine hydrochloride thus obtained (3.6 g.) was treated by the previous procedure. Yield of crystals with greenish luster was 2.3 g. (80%), dec. pt. above 250°.

Anal. Calcd. for $C_{25}H_{18}N_4OCl_2$: C, 65.08; H, 3.93; N, 12.15; Cl, 15.37. Found: C, 65.29; H, 4.16; N, 12.09; Cl, 15.22.

Hydrogenation of 4′-chloro-5-methoxy-2-nitrodiphenylamine with palladium catalyst and subsequent oxidation gave a compound corresponding to the product from 2-amino-5-methoxydiphenylamine.

The hydrochloride was obtained as plates with a golden green luster.

Anal. Calcd. for $C_{25}H_{18}N_4OCl_2 \cdot HCl \cdot 0.5H_2O$: C, 59.24; H, 3.98; Cl, 20.98. Found: C, 59.36; H, 4.01; Cl, 20.82.

2-Amino-3,5-dihydro-7-fluoro-5-phenyl-3-phenyliminophenazine.—To the solution obtained by hydrogenating 5 g. of 5-fluoro-2-nitrodiphenylamine in 150 ml. of 95% ethanol was added 2.3 ml. of hydrochloric acid and an oxidizing solution containing 14 g. of ferric chloride hexahydrate in 150 ml. of water. After stirring for 90 min., the hydrochloride of the crude product was precipitated by the addition of water, isolated, dissolved in methanol, and precipitated as the free base with ammonium hydroxide. The 3.2 g. of product thus obtained was chromatographed on alumina (500 g. of Merck with 10 wt. % of water added) with benzene. The main reddish brown band was eluted and rechromatographed on more active alumina. Upon recrystallizing twice from benzene, the yield of dark brown crystals was 1.65 g. (40%), dec. pt. 250–252°.

Anal. Calcd. for $C_{24}H_{17}N_4F$: C, 75.77; H, 4.51; N, 14.73. Found: C, 75.84; H, 4.55; N, 14.74.

The hydrochloride was obtained as plates with greenish luster.

Anal. Calcd. for $C_{24}H_{17}N_4F \cdot HCl$: C, 69.14; H, 4.35. Found: C, 69.30; H, 4.45.

2-Amino-3,5-dihydro-7-iodo-5-phenyl-3-phenyliminophenazine.—5-Iodo-2-nitrodiphenylamine was reduced with tin–hydrochloric acid[18] and converted to the hydrochloride by gaseous hydrogen chloride precipitation in anhydrous ethyl ether. Catalytic hydrogenation was unsuccessful with this compound.

A solution of 3.4 g. of 2-amino-5-iododiphenylamine hydrochloride in 150 ml. of 95% ethanol was oxidized by stirring for 3 hr. with a solution containing 6.3 g. of ferric chloride hexahydrate in 60 ml. of water. The hydrochloride of the crude product was precipitated by the addition of water, isolated, and recrystallized from methanol; yield, 2.35 g. Conversion to the free base with ammonium hydroxide gave 1.9 g. of brown crystals which, when chromatographed on alumina (300 g. of Merck with 8 wt. % of water added) with benzene, yielded 1.3 g. (62%) of product, dec. pt. 269–272°.

Anal. Calcd. for $C_{24}H_{17}N_4I$: C, 59.02; H, 3.51; N, 11.47; I, 25.99. Found: C, 59.20; H, 3.53; N, 11.41; I, 25.86.

The hydrochloride was obtained as needles with golden green luster.

Anal. Calcd. for $C_{24}H_{17}N_4I \cdot HCl$: C, 54.92; H, 3.46. Found: C, 54.79; H, 3.53.

2-Amino-7-bromo-3,5-dihydro-5-phenyl-3-phenyliminophenazine.—To a solution obtained by hydrogenating 11.7 g. of 5-bromo-2-nitrodiphenylamine in 200 ml. of 95% ethanol was added an oxidizing solution containing 30 g. of ferric chloride hexahydrate and 2 ml. of hydrochloric acid in 30 ml. of water. After standing 48 hr., the solution was chilled, yielding 3.5 g. of crude hydrochloride. Fifteen grams of the hydrochloride thus prepared was converted with ammonium hydroxide in 95% ethanol to 8.6 g. of crude free base which in turn was chromatographed on alumina (2 kg. of Harshaw with 10 wt. % of water added) with benzene. The product obtained by elution of the main band was recrystallized twice from dichloromethane–methanol as follows. After adding an equal volume of methanol to a warm solution of the base in 300 ml. of dichloromethane, the resulting solution was reduced to 300 ml. and allowed to cool. The yield was 4.8 g., dec. pt. gradual above 200°.

Anal. Calcd. for $C_{24}H_{17}N_4Br$: C, 65.31; H, 3.88. Found: C, 65.47; H, 4.00. The hydrochloride was obtained as needles with dark green luster.

Anal. Calcd. for $C_{24}H_{17}N_4Br \cdot HCl$: C, 60.33; H, 3.80. Found: C, 60.19; H, 3.86.

2-Amino-7-chloro-3,5-dihydro-5-phenyl-3-phenyliminophenazine.—5-Chloro-2-nitrodiphenylamine was treated similarly to the bromo analog.[24]

The hydrochloride was obtained as plates with greenish luster.

Anal. Calcd. for $C_{24}H_{17}N_4Cl \cdot HCl$: C, 66.52; H, 4.19. Found: C, 66.62; H, 4.25.

2-Amino-3,5-dihydro-5-phenyl-3-phenyliminophenazine.—2-Nitrodiphenylamine was hydrogenated and the resulting diamine was precipitated as the hydrochloride from anhydrous ethyl ether with gaseous hydrogen chloride. The 2-aminodiphenylamine hydrochloride thus obtained was oxidized with ferric chloride by the procedure of Barry, *et al.*,[1] and chromatographed on alumina (3 g. of base on 700 g. of Merck with 10 wt. % of water added) with benzene. The deep red band gave, on elution and recrystallization from dichloromethane–methanol, dark red plates, dec. pt. 258–260°.

Anal. Calcd. for $C_{24}H_{18}N_4$: C, 79.53; H, 5.01. Found: C, 79.71; H, 4.84.

The hydrochloride was obtained as plates with greenish luster.

Anal. Calcd. for $C_{24}H_{18}N_4 \cdot HCl \cdot 0.5H_2O$: C, 70.66; H, 4.94; Cl, 8.69. Found: C, 70.39; H, 5.10; Cl, 8.31.

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[23] F. Kehrmann and M. Cordone, *Ber.*, **46**, 3009 (1913).

[24] *Cf.* ref. 3.

A second broad orange band resulted from 2-anilino-3,5-dihydro-3-imino-5-phenylphenazine, m.p. 200° (lit.[1] 202–203°).

Anal. Calcd. for $C_{24}H_{18}N_4$: C, 79.53; H, 5.01. Found: C, 79.60; H, 4.93.

The hydrochloride was obtained as plates with greenish luster.

Anal. Calcd. for $C_{24}H_{18}N_4 \cdot HCl$: C, 72.26; H, 4.80. Found: C, 72.22; H, 4.93.

III. Condensation of 7-Substituted 2-Amino-3,5-dihydro-5-phenyl-3-phenyliminophenazines with Cyclohexanone.—The preparation of the 7-chloro compound is given in detail. Other compounds were prepared in like manner with similar yields. All the compounds are green crystals with bluish luster which gradually decompose on heating above 220° without a distinct melting point.

The green products obtained from the II-isomers are only slightly soluble in cold benzene and dichloromethane giving green, nonfluorescent solutions, insoluble in ether and carbon tetrachloride, very sparingly soluble in water with a red color, and slightly soluble in alcohols. Concentrated alcoholic solutions are green and upon dilution became red with fluorescence. When an attempt was made to chromatograph these compounds in benzene solution on alumina (Woelm, basic, activity III), the compounds immediately changed to a red form which was adsorbed very strongly and could not be eluted with benzene. The infrared spectra of these green substances (obtained with potassium bromide pellets on the Beckman IR-4 instrument with lithium fluoride optics) do not show any bands in the region of the N–H stretch frequencies, thus indicating that all the amino groups were fully substituted. The elementary analyses correspond to 1:1 condensation products between the parent II-isomers and cyclohexanone with the elimination of one molecule of water.

Addition of sodium hydroxide solution to the red alcoholic solutions of the protonated Schiff bases returns the green color. The color change occurs between pH 9 and 12 depending on the nature of the 7-substituent.

7-Chloro-2-cyclohexylideneamino-3,5-dihydro-5-phenyl-3-phenyliminophenazine.—A solution of 0.20 g. of 2-amino-7-chloro-3,5-dihydro-5-phenyl-3-phenyliminophenazine, 0.5 g. of polyphosphoric acid, and 0.5 ml. of cyclohexanone (Eastman Kodak 972) in 20 ml. of 95% ethanol was refluxed for 2 hr. The red reaction mixture was made alkaline with 10% sodium hydroxide solution and the green product precipitated by the addition of water. The crude Schiff base was isolated, washed with water, dried, and repeatedly recrystallized from benzene. The yield was 0.20 g. (85%).

Anal. Calcd. for $C_{30}H_{25}N_4Cl$: C, 75.53; H, 5.28; Cl, 7.43. Found: C, 75.35; H, 5.41; Cl, 7.23.

7-Bromo-2-cyclohexylideneamino-3,5-dihydro-5-phenyl-3-phenyliminophenazine.

Anal. Calcd. for $C_{30}H_{25}N_4Br$: C, 69.08; H, 4.83; Br, 15.32. Found: C, 68.95; H, 5.10; Br, 15.63.

2-Cyclohexylideneamino-3,5-dihydro-7-fluoro-5-phenyl-3-phenyliminophenazine.

Anal. Calcd. for $C_{30}H_{25}N_4F$: C, 78.24; H, 5.47; N, 12.17. Found: C, 78.39; H, 5.59; N, 12.09.

2-Cyclohexylideneamino-3,5-dihydro-7-iodo-5-phenyl-3-phenyliminophenazine.

Anal. Calcd. for $C_{30}H_{25}N_4I$: C, 68.38; H, 4.43; N, 9.86; I, 22.33. Found: C, 63.57; H, 4.53; N, 9.90; I, 22.24.

2-Cyclohexylideneamino-3,5-dihydro-7-ethoxy-5-phenyl-3-phenyliminophenazine.

Anal. Calcd. for $C_{32}H_{30}N_4O$: C, 78.98; H, 6.21; N, 11.51; C_2H_5O, 9.26. Found: C, 78.87; H, 6.08; N, 11.55; C_2H_5O, 9.05.

Hydrogenation of a solution containing 0.15 g. of the Schiff base, 0.2 g. of palladium catalyst, and a few drops of 10% sodium hydroxide solution in 75 ml. of absolute ethanol followed by the removal of the catalyst, air reoxidation, and reduction of volume, gave, upon addition of water and some sodium hydroxide solution, a precipitate which was chromatographed with benzene on alumina (Woelm activity III). The effluent of a rapid orange band was reduced in volume, dried, and rechromatographed on activity II alumina. Recrystallization from benzene–Skellysolve B gave 0.041 g. of 2-cyclohexylamino-3,5-dihydro-7-ethoxy-5-phenyl-3-phenyliminophenazine as brown needles, m.p. 225–227°.

Anal. Calcd. for $C_{32}H_{32}N_4O$: C, 78.65; H, 6.60; N, 11.47; C_2H_5O, 9.20. Found: C, 78.39; H, 6.53; N, 11.61; C_2H_5O, 9.00.

A second brown-red band was identified by its infrared spectrum as 2-amino-3,5-dihydro-7-ethoxy-5-phenyl-3-phenyliminophenazine, the hydrolysis product of the Schiff base.

2-Cyclohexylideneamino-3,5-dihydro-7-methoxy-5-phenyl-3-phenyliminophenazine.

Anal. Calcd. for $C_{31}H_{28}N_4O$: C, 78.78; H, 5.97; CH_3O, 6.56. Found: C, 78.68; H, 6.30; CH_3O, 6.48.

A hydrogenation–reoxidation sequence similar to that described for the 7-ethoxy analog gave, from 0.31 g. of Schiff base, 0.056 g. of 2-cyclohexylamino-3,5-dihydro-7-methoxy-5-phenyl-3-phenyliminophenazine, m.p. 218–220°.

Anal. Calcd. for $C_{31}H_{30}N_4O$: C, 78.44; H, 6.37; N, 11.81; CH_3O, 6.54. Found: C, 78.43; H, 6.37; N, 11.91; CH_3O, 6.60.

2-Cyclohexylideneamino-3,5-dihydro-5-phenyl-3-phenyliminophenazine.

Anal. Calcd. for $C_{30}H_{26}N_4O$: C, 81.42; H, 5.92; N, 12.66. Found: C, 81.33; H, 5.87; N, 12.62.

Others.—Similar green products were obtained when the oxidation products of 2-amino-4′,5-dimethoxydiphenylamine, 2-amino-4′-fluoro-5-methoxydiphenylamine, and 2-amino-4′-chloro-5-methoxydiphenylamine were reacted with cyclohexanone in the manner described. These Schiff bases, however were not analyzed.

Polarography. Materials.—The substituted phenazine hydrochlorides have been described. All inorganic reagents were reagent grade and were used without further purification. Nitrogen used for purging sample solutions free of oxygen was 99.9% dry-grade (Liquid Carbonic Corp.) which was scrubbed with vanadous chloride solution and water.[25] The nitrogen was further conditioned by passage through a 5-ml. sample of the supporting electrolyte. Ethanol was 190 proof alcohol (U. S. Industrial Chemicals) distilled from dilute sulfuric acid, then from silver nitrate–potassium hydroxide[26] through 15-plate perforated-plate vacuum-jacketed column with a built-in electronically controlled head.[27]

Apparatus.—The polarograph was a recording instrument constructed in the Department and previously described by Crowell, *et al.*[28] The cell was of the Pecsok–Juvet type[29] and thermostated at 25.00 ± 0.05°.

The pH data were obtained with a Beckman Model G pH meter in conjunction with a Beckman 40498 glass electrode immersed in the solutions compartment and using the cell calomel electrode. The assembly was standardized against Beckman buffer solutions.

Solutions.—The polarograms were obtained in 3:1 95% ethanol–aqueous buffer mixtures. The buffer solutions were sodium acetate–nitric acid systems prepared analogously to Walpole's[30] sodium acetate–hydrochloric acid solutions. The total acetate concentration was 0.2 F and appropriate amounts of lithium nitrate were added to increase the ionic strength to 1 M.

The ethanolic solutions were 0.333 mF in the organic compound. Hence, on 3:1 dilution, the resulting solutions were nominally 0.25 mF in the phenazine derivative and 0.25 M in ionic strength. No corrections were made for the volume contractions.

Polarogram Measurements.—The half-wave potentials were obtained graphically using the maxima of the oscillations. Buffer blanks were used to estimate the residual current when in the region of the mercury dissolution potential. The precision of the graphical data was about ±2 mv.

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