stirring. An additional 60 ml. of water was then added in one portion and stirring was continued for 20 minutes. The mixture was then allowed to stand until the liquid layers had separated, and the upper toluene layer was decanted and discarded. The lower aqueous slurry was then filtered with suction. The resulting cake of crude product was removed from the funnel, slurried with 250 ml. of water and the slurry was again filtered. The cake was then digested with 200 ml. of boiling 95% ethanol and the slurry was filtered hot, washed with cold 95% ethanol and dried in the vacuum oven at 55°. The resulting crude product weighed 66 g., m.p. 220–222° dec. The purity by titration with standard iodine solution was 95%. It was purified by solution in dilute aqueous sodium hydroxide, treatment with decolorizing carbon, filtration and reprecipitation by acidification with acetic acid. After filtration, washing with water and drying, the purified product weighed 62.3 g. (81.6% of theory), m.p. 228–230° dec.; purity by iodine titration, 98.2%.

5-Iodo-2-thiouracil Monosodium Salt Monohydrate.—A solution of 4.4 g. (0.11 mole) of sodium hydroxide in 89 ml. of water was heated to 65° and to it was added 35.4 g. (0.1 mole) of 5-iodo-2-thiouracil. The mixture was stirred at 65–70° until solution was complete. The solution was then treated with decolorizing carbon and the mixture was filtered hot. The filtrate was cooled slowly to 5° and the resulting crop of white crystals was collected on a Büchner funnel. It was washed with 10 ml. of ice-water, then with 15 ml. of ice-cold 95% ethanol and 20 ml. of ether. After drying for 18 hours in a vacuum oven at 50° the product had the composition of the monosodium salt monohydrate. The yield was 25.4 g. or 86.5%, m.p. 235° dec.; purity by iodine titration, 99.4% as monosodium salt monohydrate.

Anal. Calcd. for $C_4H_4N_2O_2ISNa$: N, 9.52; I, 43.16. Found: N, 9.61; I, 43.15.

Acidification of the mother liquor from the salt preparation yielded 1.65 g. (6.5%) of recovered 5-iodo-2-thiouracil. According to the same procedure, monosodium salts of the following compounds were prepared from the corresponding 5-iodo-2-thiouracils.

(1) 6-Methyl-5-iodo-2-thiouracil[4]: Obtained as the monohydrate; yield 66%, m.p. 233° dec.; purity by iodine titration, 100%. *Anal.* Calcd. for $C_5H_6N_2O_2ISNa$: N, 9.09; I, 41.20. Found: N, 9.02; I, 41.55.

(2) 6-Ethyl-5-iodo-2-thiouracil: yield 70%, m.p. 234–235° dec. *Anal.* Calcd. for $C_6H_6N_2OISNa$: N, 9.21; I, 41.74. Found: N, 9.34; I, 41.93.

(3) 6-*n*-Propyl-5-iodo-2-thiouracil: yield 83%, m.p. 215–216° dec. *Anal.* Calcd. for $C_7H_8N_2OISNa$: N, 8.81; I, 39.89. Found: N, 8.58; I, 40.02.

SUMMIT, NEW JERSEY

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF DOJINDO & CO., LTD., AND THE INSTITUTE OF APPLIED CHEMISTRY, KYUSHU UNIVERSITY, JAPAN]

Polyazobenzenes. II. Synthesis and Ultraviolet Absorption Spectra of Polyazobenzenes Containing Nitro, Amino and Hydroxyl Groups

BY KEIHEI UENO[1] AND SABURO AKIYOSHI

RECEIVED JANUARY 14, 1954

Polyazobenzenes containing nitro, amino and hydroxyl groups and polyazostilbenes were synthesized and their ultraviolet absorption spectra determined.

In order to study the effect of substituents on the absorption spectra of polyazobenzenes, a number of polyazobenzenes with nitro, amino and hydroxyl groups, and of azostilbenes have been synthesized and their absorption spectra determined.

Hartley[2a] and Brode[2b] reported that the absorption spectra of substituted azobenzenes, especially those having amino or hydroxyl groups in the *para* position, are considerably affected by light because of their photochemical *cis–trans* isomerism. The higher *p*-substituted polyazo homologs have similar phototropic properties. The phototropism of unsubstituted polyazobenzenes is so slow that the pure *trans* isomers could be obtained by chromatographic separation,[3] but the pure *trans* form of substituted polyazobenzenes could not be obtained by this method. In this study, therefore, the absorption spectra were determined on benzene solutions of the polyazobenzenes, which were kept in the dark and which were believed to contain mainly the *trans* forms.[2]

Experimental

The polyazobenzenes were synthesized as previously reported,[3] by condensation of nitronitrosobenzene with an amino compound, followed by reduction of the nitro group. Some polyazophenols were prepared by the coupling of diazotized amines with phenol. In the case of the azostilbenes, nitronitroso- or nitrosobenzene was condensed with aminostilbene in glacial acetic acid. All the compounds studied are listed in Tables I, II and III.

4-Phenylazo-4′-nitroazobenzene (II). (a) **From 4-Aminoazobenzene.**—Hot solutions of 3.8 g. of 4-aminoazobenzene in 20 ml. of glacial acetic acid and 3.2 g. of *p*-nitronitrosobenzene in 20 ml. of glacial acetic acid were mixed. After a few minutes, the mixture became nearly solid due to the formation of 4-phenylazo-4′-nitroazobenzene, which was recrystallized from glacial acetic acid and then from nitrobenzene. The orange crystals, m.p. 223.5–224.5°, weighed 4.2 g.

(b) **From 4-Nitro-4′-aminoazobenzene.**—A mixture of 0.5 g. of 4-nitro-4′-aminoazobenzene (m.p. 210–212°)[4] dissolved in 10 ml. of glacial acetic acid and 0.2 g. of nitrosobenzene in glacial acetic acid was kept at room temperature for two days. The crystals, recrystallized as above, weighed 0.4 g. A mixed melting point of both samples showed no depression.

Anal. Calcd. for $C_{18}H_{13}O_2N_5$: N, 21.13. Found: N, 21.09.

4-Phenylazo-4′-aminoazobenzene (VIII).—A suspension of 2.0 g. of the nitroazo compound (II) in 20 ml. of ethanol was heated on a water-bath with 5 ml. of 30% NaSH in 5 ml. of water for 15 minutes. After cooling, an equal volume of water was added and the solid material separated. After initial purification as the hydrochloride, the free amine was recrystallized from toluene to give orange crystals; 1.0 g., m.p. 186–187°.[5] They dissolved in concentrated sulfuric acid to give a red solution which turned violet.

Anal. Calcd. for $C_{18}H_{15}N_5$: N, 23.24. Found: N, 22.90.

4-Phenylazo-4′-(*p*-nitrophenylazo)-azobenzene (III) and **4-Phenylazo-4′-(*p*-aminophenylazo)-azobenzene** (IX).—These compounds were synthesized from 4-phenylazo-4′-

---

(1) Department of Chemistry, Clark University, Worcester, Mass.

(2) (a) G. S. Hartley, *Nature*, **140**, 281 (1937); *J. Chem. Soc.*, 633 (1938); (b) W. R. Brode, J. H. Gould and G. M. Wyman, THIS JOURNAL, **74**, 4641 (1952).

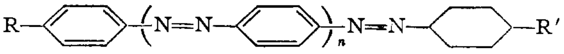
(3) K. Ueno, THIS JOURNAL, **74**, 4508 (1952).

(4) German Patent 134,860; *Frdl.*, **16**, 873 (1900).

(5) The material reported by R. Nietzki and J. Diesterweg, *Ber.*, **21**, 2146 (1888), is quite different from our sample. Its structure is doubtful because it failed to give the expected 4-phenylazoazobenzene upon deamination.

TABLE I

ABSORPTION DATA OF POLYAZOBENZENES OF THE TYPE

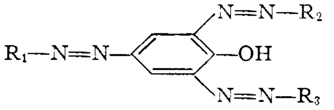


	n	R	R'	M.p., °C.	λ_{1max}	$\epsilon_1 \times 10^{-3}$	λ_{2max}	$\epsilon_2 \times 10^{-3}$
I	0	H	NO_2	134–135[a]	425–426	0.9	338	25.8
II	1	H	NO_2	223.5–224.5			376	44.1
III	2	H	NO_2	272.5–273			399	64.1
IV	0	NO_2	NO_2	221–222[b]	472	0.6	338	26.8
V	1	NO_2	NO_2	253–254[c]			377	48.3
VI	2	NO_2	NO_2	282–283[d,e]			402–404	67.1
VII	0	H	NH_2	123–124[f]			378	24.0
VIII	1	H	NH_2	186–187			416	39.0
IX	2	H	NH_2	231–232			428	49.1
X	0	NH_2	NH_2	248–249[d]			397	28.5
XI	1	NH_2	NH_2	255–256[c]			430–432	45.6
XII	2	NH_2	NH_2	295–296[g,h]			448	51.6
XIII	0	H	OH	153.5–154[i]	440–442	0.8	346	25.0
XIV	1	H	OH	184–185[j]			383	40.8
XV	2	H	OH	222–224			400–401	49.5
XVI	0	NH_2	OH	185–186[k]			379–380	28.8
XVII	1	NH_2	OH	217–218			418–420	42.0
XVIII	2	NH_2	OH	253–254			438	52.5

[a] G. Charrier and A. Beretta, *Gazz. chim. ital.*, **54**, 977 (1924). [b] A. Weiner and E. Stiasny, *Ber.*, **32**, 3258 (1899). [c] P. Ruggli and E. Iselin, *Helv. Chim. Acta*, **30**, 739 (1947). [d] O. N. Witt and E. Kopetschni, *Ber.*, **45**, 1134 (1912). [e] A. G. Green and E. A. Bearder, *J. Chem. Soc.*, 1971 (1911). [f] W. R. Brode, J. H. Gould and G. M. Wyman, THIS JOURNAL, **74**, 4641 (1952). [g] P. Ruggli and C. Petitjean, *Helv. Chim. Acta*, **21**, 711 (1938). [h] A. G. Green and F. M. Rowe, *J. Chem. Soc.*, 2003 (1912). [i] W. R. Brode and L. E. Herdle, *J. Org. Chem.*, **6**, 713 (1941). [j] Beilstein, "Hand. d. org. Chem.," E. I. Vol. XVI, p. 238. [k] R. Meldola, *J. Chem. Soc.*, 658 (1885).

TABLE II

ABSORPTION DATA OF POLYAZOPHENOLS OF THE TYPE

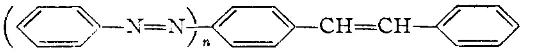


	R_1	R_2	R_3	M.p., °C.	λ_{1max}	$\epsilon_1 \times 10^{-3}$	λ_{2max}	$\epsilon_2 \times 10^{-3}$
XIX	H	Phenyl	H	81–82[j]	386–387	9.8	326–327	18.8
XX	Phenyl	Phenyl	H	130–131[l]			342–343	43.3
XXI	Phenyl	Phenyl	Phenyl	216–216.5[m]		11.6	342	55.1
XXII	Tolyl	H	H	150–150.5[n]	434	1.1	350	28.6
XXIII	Tolyl	Phenyl	H	135–136	434		348	45.0
XXIV	Phenyl	Tolyl	H	118–119[o]			351	45.6
XXV	Tolyl	Tolyl	H	169–170[p]			351–353	47.6
XXVI	Tolyl	Phenyl	Phenyl	207–208	434–438	11.2	344–345	56.5

[l] H. H. Hodgson and E. Marsden, *J. Chem. Soc.*, 379 (1943). [m] E. Grundmougin and H. Freimann, *Ber.*, **40**, 2662 (1907). [n] E. Grundmougin and H. Freimann, *J. prakt. Chem.*, [2] **78**, 392 (1908). [o] P. Griess, *Ber.*, **9**, 628 (1876). [p] H. Goldschmidt and A. Pollak, *ibid.*, **25**, 1325 (1892).

TABLE III

ABSORPTION DATA OF AZOSTILBENES OF THE TYPE



	n	M.p., °C.	λ_{max}	$\epsilon \times 10^{-3}$
XXVII	1	190–191	372–374	34.0
XXVIII	2	213–215	394–395	52.0

aminoazobenzene by a method analogous to that described above. III was obtained as brown crystals, m.p. 272.5–273°, by repeated recrystallization of the crude condensation product.

Anal. Calcd. for $C_{24}H_{17}O_2N_7$: N, 20.20. Found: N, 20.60.

IX was obtained as dark red crystals by purification of the crude product as the hydrochloride followed by recrystallization of the free base from toluene, m.p. 231–232°.[6]

Anal. Calcd. for $C_{24}H_{10}N_7$: N, 24.18. Found: N, 24.52.

1,4-Bis-(*p*-nitrophenylazo)-benzene (V).—This compound was more easily synthesized by the condensation of 4-nitro-4'-aminoazobenzene[4] with *p*-nitronitrosobenzene in glacial acetic acid than by the method reported in the literature. Reddish-violet crystals, recrystallized from nitrobenzene, melted at 253–254°; m.p. reported 252–253°.[7]

1,4-Bis-(*p*-aminophenylazo)-benzene (XI).—This compound, which had been previously prepared with great difficulty, was synthesized by simple reduction of the pure dinitro compound V. Red-violet needles, recrystallized from xylene, melted at 255–256°; m.p. reported 256–257°.[7]

4-(*p*-Aminophenylazo)-4'-oxyazobenzene (XVII).—XVII was obtained by reduction of the corresponding nitro compound, which was synthesized by the following two methods: (a) From 4-nitro-4'-aminoazobenzene: The diazotized solution from 0.4 g. of 4-nitro-4'-aminoazobenzene[4] was mixed with 0.2 g. of phenol in pyridine–water (1:1). The resulting crystals were separated and recrystallized from nitrobenzene to give the nitro compound as red-brown crystals; 0.42 g., m.p. 253–254°. (b) From 4-amino-4'-oxyazobenzene: The same compound was obtained by the

---

(6) S. Dutt, *J. Chem. Soc.*, 1171 (1926), synthesized this compound by coupling diazotized 4-phenylazo-4'-aminoazobenzene with aniline; we could not reproduce his results and his sample was quite different from ours. The structure of his material is questionable since it was prepared from VIII the identity of which was doubtful.

(7) See Table I, footnote *c*.

reaction of 4-amino-4′-oxyazobenzene (0.4 g.) and *p*-nitronitrosobenzene (0.3 g.) in glacial acetic acid; it gave the same melting point after recrystallization from nitrobenzene. Reduction of the nitro compound was carried out as described above. Recrystallization from absolute ethanol gave 4-(*p*-aminophenylazo)-4′-oxyazobenzene as dark brown crystals, m.p. 217–218°.

Anal. Calcd. for $C_{18}H_{19}ON_5$: N, 22.08. Found: N, 22.03.

4-Phenylazo-4′-(*p*-oxyphenylazo)-azobenzene (XV).—XV was easily obtained by the condensation of nitrosobenzene with 4-(*p*-aminophenylazo)-4′-oxyazobenzene (XVII) in glacial acetic acid. Recrystallization from nitrobenzene gave dark brown crystals, m.p. 222–224°.[8]

Anal. Calcd. for $C_{24}H_{18}ON_6$: N, 20.68. Found: N, 21.05.

4-(*p*-Aminophenylazo)-4′-(*p*-oxyphenylazo)-azobenzene (XVIII).—The amino compound (XVII) was condensed with *p*-nitronitrosobenzene and then reduced by the method described above. Recrystallization from benzene yielded dark red crystals, m.p. 253–254°.

Anal. Calcd. for $C_{24}H_{19}ON_7$: N, 23.26. Found: N, 22.49.

2-Phenylazo-4-(*p*-tolylazo)-phenol (XXIII) and 2,6-Bisphenylazo-4-(*p*-tolylazo)-phenol (XXVI).—These polyazophenols were obtained by the coupling of stoichiometric amounts of benzenediazonium chloride with *p*-tolylazophenol in sodium hydroxide solution. XXIII was obtained as brown-yellow crystals, m.p. 135–136°,[9] after recrystallization from ethanol–acetic acid (1:1).

Anal. Calcd. for $C_{19}H_{16}ON_4$: N, 17.71. Found: N, 18.15.

XXVI was also isolated as brown crystals, m.p. 207–208°, after recrystallization from nitrobenzene.

Anal. Calcd. for $C_{25}H_{20}ON_6$: N, 19.99. Found: N, 19.54.

4-Styrylazobenzene (XXVII) and 4-Styryl-4′-phenylazoazobenzene (XXVIII).—These compounds were synthesized from *trans*-4-aminostilbene[10] by a method analogous to that used for the polyazo compounds. XXVII was obtained as light brown crystals, m.p. 191° after recrystallization from glacial acetic acid.

Anal. Calcd. for $C_{20}H_{16}N_2$: N, 9.86. Found: N, 9.62.

The brown crystals of XXVIII melted at 213–215° after recrystallization from nitrobenzene.

Anal. Calcd. for $C_{26}H_{20}N_4$: N, 14.42. Found: N, 14.56.

Preparation of Solutions.—A weighed sample was dissolved in freshly distilled benzene and stored in the dark for at least 12 hours.

Measurement of Absorption Spectra.—Absorption spectra were measured with a Beckman model DU-2 spectrophotometer and matched silica cells. The measurements were carried out as rapidly as possible in the dark with the aid of a red lamp. Thus it was possible to obtain nearly reproducible results.

Results

The characteristics of the ultraviolet absorption spectra of *para* substituted *p*-polyazobenzenes are quite similar to those of unsubstituted *p*-polyazobenzenes; both series of compounds have a strong main band (K band) and a weak band (R band) in the region from 600 to 280 mμ which is observable in benzene solution. But since the weak R band is usually masked by the bathochromic shift of the K band in higher homologs of *p*-polyazobenzenes, only a single strong band is observed in this region. The absorption data are given in Table I. The bathochromic shift of this linear conjugated system is quite similar to that of the *p*-polyphenyls.[11] The plot of λ_{max}^2 against the number of azo groups is shown in Fig. 1.

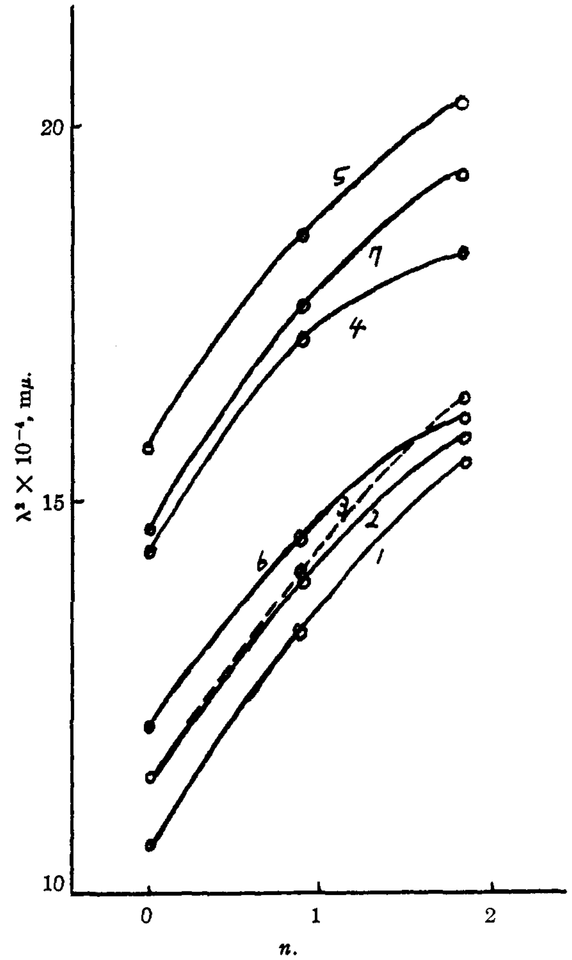
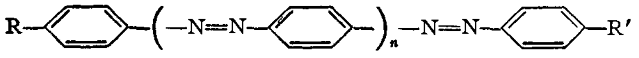


Fig. 1.—Relation between the wave length of absorption maxima and the number of azo linkage.



	R	R′		R	R′
1.	H	H	5.	NH_2	NH_2
2.	H	NO_2	6.	H	OH
3.	NO_2	NO_2	7.	NH_2	OH
4.	H	NH_2			

The bathochromic power of *para* substituents is the order $NH_2 > OH > NO_2$, as expected. The 4-amino-*p*-polyazobenzenes exhibit different absorption bands in benzene than in alcohol solution[12]; strong bathochromic shift observed in alcohol is probably due to the strong hydrogen solvation effect of the solvent.

As Table III shows the absorption spectra of the azostilbenes are similar to those of the *p*-polyazobenzenes; they both have a single strong band in the region observed, but the extinction coefficients of the *p*-phenylazostilbenes are somewhat lower. It is interesting that the wave lengths of the main absorption band of azobenzene (321 mμ) and stilbene (295 mμ) are quite different.

---

[8] This compound was reported by Dutt, but its identity is not clearly established for the reasons mentioned in footnote 6.

[9] Reported melting point of 115–116° is probably a misprint (H. Goldschmidt and A. Pollak, *Ber.*, **25**, 1325 (1892)).

[10] R. Stoermer and H. Oehlert, *Ber.*, **55**, 1239 (1922).

[11] L. Ferguson, *Chem. Revs.*, **43**, 385 (1948).

[12] H. Dahn and H. N. Castelmur, *Helv. Chim. Acta*, **36**, 638 (1953).

The absorption spectra of polyazophenols, in which more than one phenylazo group is attached to a single phenol ring, are quite different from those of *p*-polyazophenols, which have linear conjugated systems. Some of the former have been studied in methanol solution.[13] Our results on benzene solution (Table II) are almost the same with minor exceptions. The introduction of a methyl group in the position *para* to the phenylazo group causes a bathochromic and hypochromic shift, which is greater for a 2-phenylazo group than for a 4-phenylazo group.

Acknowledgment.—The authors are grateful to Mr. Yasuto Yamaguchi for his assistance in the synthetic work and to Prof. A. E. Martell of Clark University for his kindness in reading the manuscript.

KUMAMOTO, JAPAN

(13) W. R. Brode and L. E. Herdle, *J. Org. Chem.*, **6**, 713 (1941).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF DOJINDO & CO., LTD., AND THE INSTITUTE OF APPLIED CHEMISTRY, KYUSHU UNIVERSITY, JAPAN]

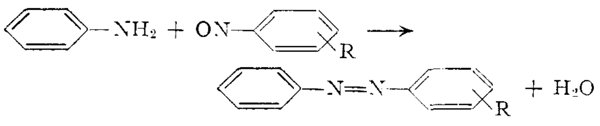
Kinetic Study on the Condensation Reaction of Aniline and Nitrosobenzenes

BY KEIHEI UENO[1a] AND SABURO AKIYOSHI

RECEIVED JANUARY 14, 1954

The rates of condensation reactions of aniline with nitrosobenzene and its derivatives were measured spectrophotometrically, and the differences in reactivity of the nitrosobenzenes discussed. The apparent energies of activation of these reactions were also determined.

In an investigation of the synthesis and absorption spectroscopy of polyazobenzenes,[1b] it was found that the rate of condensation of *p*-nitronitrosobenzene with aniline to form *p*-nitroazobenzene was far greater than that of nitrosobenzene with aniline to form azobenzene. In this paper we are reporting the kinetics of the condensation reactions of aniline with nitrosobenzene and with its nitro and chloro derivatives, the simplest examples of the general reaction



R = H; *p*-, *m*-, *o*-NO_2; or *p*-Cl

The rate of formation of azobenzenes can easily be followed spectrophotometrically because of the great difference in absorption between the reactants, aniline and the nitrosobenzenes, and the products, azobenzenes.

The initial optical density is expressed as

$$D_0 = \epsilon_a a + \epsilon_b b \tag{1}$$

where ϵ_a and ϵ_b are the molecular extinction coefficients of aniline and nitrosobenzene, respectively, and *a* and *b* their initial molar concentrations. Then, at any time *t*, the optical density of the reaction mixture is

$$D_t = \epsilon_a(a - x) + \epsilon_b(b - x) + \epsilon_c x \tag{2}$$

where *x* is the molar concentration of the azobenzene formed, and ϵ_c the molecular extinction coefficient of azobenzene. From equations 1 and 2, *x* can be calculated as

$$x = \frac{D_t - D_0}{\epsilon_c - (\epsilon_a + \epsilon_b)} \tag{3}$$

In the above discussion it was assumed that all components obey Beer's law. Measurement of the optical densities of the individual components at 320–340 mμ (Table I) showed that light absorption by aniline is almost negligible, so that equation 3 may be simplified to

$$x = \frac{D_t - D_0}{\epsilon_c - \epsilon_b} \tag{4}$$

TABLE I

MOLECULAR EXTINCTION COEFFICIENTS OF ANILINE, NITROSOBENZENES AND AZOBENZENES

	$\epsilon \times 10^{-3}$		
	320 mμ	330 mμ	340 mμ
Aniline		Negligible	
Nitrosobenzene	4.44	2.11	0.85
p-Nitronitrosobenzene	3.78	...	2.12
m-Nitronitrosobenzene	2.05	1.12	0.54
o-Nitronitrosobenzene	3.16	...	1.36
p-Chloronitrosobenzene	10.25	...	2.28
Azobenzene	21.34	19.45	12.89
p-Nitroazobenzene	23.14	25.71	24.78
m-Nitroazobenzene	16.31	14.33	10.39
o-Nitroazobenzene	18.12	16.90	13.47
p-Chloroazobenzene	23.80	23.80	20.75

Experimental

Materials.—Aniline was freshly distilled over zinc dust. Nitrosobenzene (m.p. 67.5–68°),[2] *p*-nitronitrosobenzene (119–119.5°),[3] *m*-nitronitrosobenzene (89.5–90°),[3] *o*-nitronitrosobenzene (122°),[3] *p*-chloronitrosobenzene (88.5–89°),[4] *p*-nitroazobenzene (134–135°),[5] *m*-nitroazobenzene (96–96.5°),[5] *o*-nitroazobenzene (70–70.5°)[3] and *p*-chloroazobenzene (90–90.5°)[6] were prepared as described in the literature. Azobenzene was purified by recrystallizing the commercial sample from dilute ethanol and then from petroleum ether, m.p. 67.5–68°.

The glacial acetic acid and methanol were reagent grade and their optical transparency was checked over the range of wave length observed.

Samples of the stock solution of each component in glacial acetic acid were diluted with methanol to concentrations ranging from 10^{-4} to 10^{-5} mole/l., and the optical densities measured, they all obeyed Beer's law within the experimental error. The molecular extinction coefficients of each component are given in Table I.

---

(1) (a) Department of Chemistry, Clark Univ., Worcester, Mass.; (b) K. Ueno, THIS JOURNAL, **74**, 4508 (1952).

(2) *Org. Syntheses*, **25**, 80 (1945).

(3) E. Bamberger and R. Hübner, *Ber.*, **36**, 3809 (1903).

(4) Y. Tsuzuki, T. Uemura and N. Hirasawa, *J. Chem. Soc. Japan*, **62**, 85 (1941).

(5) G. Charrier and A. Beretta, *Gazz. chim. ital.*, **54**, 977 (1924).

(6) P. Jacobson and A. Loeb, *Ber.*, **36**, 4090 (1903).