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The Synthesis of Some 4,4'-Disubstituted-2,2'-Biquinolines (I)

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2,2'-Biquinoline dioxide and 4,4'-dichloro-2,2'-biquinoline have been used for the preparation of the following 4,4'-disubstituted-2,2'-biquinolines: dimethoxy, diethoxy, dihydroxy, dipiperidino, dipyrrolidino, dibromo, diphenoxy, dithiophenoxy, di(*p*-chlorophenoxy), di(*p*-bromophenoxy), di(*p*-fluorophenoxy), di(β -naphthoxy) and the dinitro dioxide. Molar extinction coefficients have been determined for several of the copper (I) complexes of these compounds.

It is well known that 2,2'-biquinoline and certain of its derivatives give intense purple colors with cuprous ion (2,3). It has been shown by Smith and Wilkens (4) that substituents in the 4- and 4'-positions have a profound effect upon the magnitude of the molar extinction coefficients of the cuprous complexes of similar compounds. However, few 2,2'-biquinolines exclusively substituted in the 4,4'-positions have hitherto been available. These have been limited to some alkyl (5,6) and aryl (7) substituted biquinolines and to some amido derivatives of bicinchoninic (6) acid. In general symmetrical 2,2'-biquinolines have been prepared by the Ullmann reaction (7) by the method of Ueda (6,8,9,10) and by the coupling of certain quinolines over palladium-on-charcoal (11) or Raney nickel (12). Unsymmetrical 2,2'-biquinolines have been synthesized by the Friedländer reaction (7,13).

The excellent work of Ochiai and his coworkers (14), who prepared 4-substituted pyridines from pyridine *N*-oxides, suggested to us that such a route might prove to be successful in synthesizing 4,4'-disubstituted 2,2'-biquinolines. Accordingly, 2,2'-biquinoline was oxidized to the dioxide (I) by the method of Nakano (6). Treatment of I with concentrated nitric and sulfuric acids (Ochiai's method (14)) led to a tetranitro dioxide of unknown structure, rather than to the expected 4,4'-dinitro-2,2'-biquinoline dioxide (II). However II was successfully prepared by the nitration of I in concentrated nitric acid alone. 4,4'-Dichloro-2,2'-biquinoline (III) was synthesized by two methods. The first method involved the displacement of the nitro groups of II by chlorine, using acetyl chloride, followed by deoxygenation of the di-*N*-oxide with phosphorus trichloride in chloroform. In the second procedure the chloro groups were introduced directly into the 4,4'-positions of I by the use of phosphoryl chloride.

This was accompanied by simultaneous deoxygenation. Meisenheimer (15) reported that the treatment of quinoline-*N*-oxide with phosphoryl chloride led to a mixture of 2- and 4-chloroquinolines. 4,4'-

Dimethoxy-2,2'-biquinoline (IV) was also prepared by two methods. The first procedure was the conventional one wherein the nitro groups of II were displaced with sodium methoxide followed by deoxygenation of the *N*-oxygens with phosphorus trichloride. The intermediate di-*N*-oxide was not isolated. IV was also obtained by the treatment of 4-methoxyquinoline-*N*-oxide with palladium on carbon at elevated temperatures. This was the first time that an *N*-oxide had been used in this type of coupling reaction. The crude product was treated with phosphorus trichloride in order to deoxygenate the presumably formed di-*N*-oxide, but it was later discovered that this treatment was unnecessary as deoxygenation had taken place during the course of the coupling reaction. This was evidenced by the intense purple color that a chloroform extract of the crude product gave with cuprous ion without phosphorus trichloride treatment. Biquinoline dioxides do not give this characteristic test with cuprous ion.

The fact that IV was obtained in this way from the known 4-methoxyquinoline and also from the dinitrobiquinoline dioxide proves the structure of the latter to be the 4,4'-dinitro oxide, and all subsequent derivatives to be 4,4'-substitution products.

4,4'-Diethoxy-2,2'-biquinoline (V) was prepared by the reaction of II with sodium ethoxide followed by reduction with phosphorus trichloride. 4,4'-Dibromo-2,2'-biquinoline (VI) was obtained by the reaction of II with phosphorus tribromide, the *N*-oxygens being removed during the course of the reaction. Under suitable conditions the phosphorus halide has been used to deoxygenate 4-nitroquinoline-*N*-oxide, leaving the nitro groups intact (16). However, when this method was applied to II we obtained largely VI.

The convenient method of preparation of III found by us (by the reaction of I with phosphoryl chloride) provided a suitable starting material for the preparation of various substituted 2,2'-biquinolines by nucleophilic displacement reactions. Thus, 4,4'-

diphenoxy-2,2'-biquinoline (VII) was prepared by the reaction of sodium phenoxide with III. Similarly 4,4'-dithiophenoxy-2,2'-biquinoline (VIII) was prepared by the action of III with thiophenol. 4,4'-Dipiperidino- (IX) and 4,4'-dipyrrolidino (X) 2,2'-biquinolines were synthesized by the reaction of III with the respective bases. 4,4'-Di(*p*-fluorophenoxy)- (XI), 4,4'-di(*p*-chlorophenoxy)- (XII), 4,4'-di(*p*-bromophenoxy) (XIII) and 4,4'-di(β -naphthoxy)- (XIV) 2,2'-biquinolines were prepared by reactions similar to that used for the preparation of VII. 4,4'-Dihydroxy-2,2'-biquinoline (XV) resulted from the acid hydrolysis of III.

We were unable to prepare 4,4'-diiodo- or 4,4'-difluoro-2,2'-biquinolines by displacement reactions involving iodide or fluoride ion on III. Similarly we failed in attempts to prepare 4,4'-dinitro-2,2'-biquinoline by the deoxygenation of II. The reaction of II with phosphorus trichloride, as expected led to III, and the reaction of II with phosphorus tribromide led, as previously stated, to VI.

The following molar extinction coefficients derived from Beer's law plots were determined for the copper (I) complexes of: 2,2'-biquinoline (6313); IV (7060); V (7120); and IX (11053). The wavelengths of maximum absorption were 550, 538, 540, and 554 millimicrons, respectively.

Preliminary tests indicate that XV will complex copper (I) in concentrated alkaline solutions.

EXPERIMENTAL

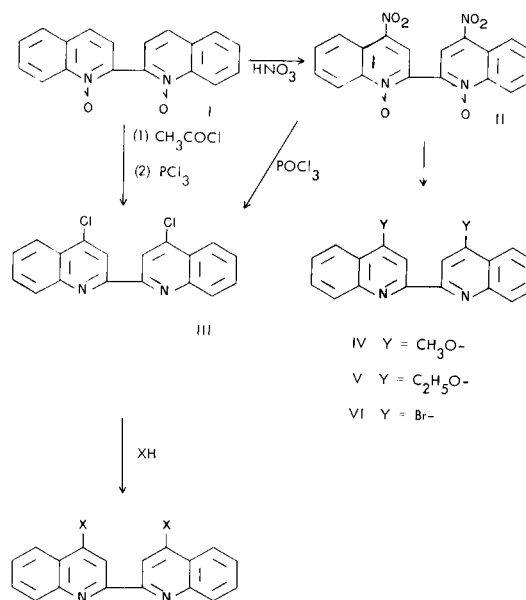
2,2'-Biquinoline Dioxide.

The procedure was similar to that of Nakano (6), except that the pure product, crystallized from methanol (m.p. 257 dec.), was not hydrated like Nakano's (m.p. 246.5-248°) as shown by infrared spectra.

4,4'-Dinitro-2,2'-biquinoline Dioxide.

2,2'-Biquinoline dioxide (9.4 g.) was heated with 125 ml. of concentrated nitric acid (density 1.42) for 3 hours at 80-90°. The solution was poured into 300 ml. of ice water, the resulting precipitate filtered,

TABLE I



IV Y = CH₃O-
V Y = C₂H₅O-
VI Y = Br-

VII X = C₆H₅O-
VIII X = C₆H₅S-
IX X = piperidino-
X X = pyrrolidino-
XI X = *p*-FC₆H₄O-
XII X = *p*-ClC₆H₄O-
XIII X = *p*-BrC₆H₄O-
XIV X = β -naphthoxy-
XV X = HO-

TABLE II

Molar Extinction Coefficients of Various Cu(I) Complexes

Compound	μ (max)	Concentration (M. P. L.)	Absorptivity	Molar Extinction Coefficient
2,2'-Biquinoline	550	9.96 x 10 ⁻⁵	0.630	6313
		4.98 x 10 ⁻⁵	0.316	
		2.49 x 10 ⁻⁵	0.159	
4,4'-Dimethoxy-2,2'-biquinoline	538	9.96 x 10 ⁻⁵	0.710	7060
		4.98 x 10 ⁻⁵	0.354	
		2.49 x 10 ⁻⁵	0.175	
4,4'-Diethoxy-2,2'-biquinoline	540	9.96 x 10 ⁻⁵	0.710	7120
		4.98 x 10 ⁻⁵	0.357	
		2.49 x 10 ⁻⁵	0.178	
4,4'-Dipiperidino-2,2'-biquinoline	554	4.98 x 10 ⁻⁵	0.543	11,053
		2.49 x 10 ⁻⁵	0.275	
		1.25 x 10 ⁻⁵	0.142	

washed with water, then with 10% sodium carbonate and finally with water. The yield of 4,4'-dinitro-2,2'-biquinoline dioxide was 2.7 g. (21%) melting at 285-290°, dec. An analytical sample prepared by recrystallization from aqueous dimethylformamide melted at 290°, dec. *Anal.* Calcd. for $C_{18}H_{10}N_4O_6$: C, 57.15; H, 2.66. Found: C, 57.45; H, 2.65.

4,4'-Dimethoxy-2,2'-biquinoline. (A) From 4,4'-Dinitro-2,2'-biquinoline Dioxide.

4,4'-Dinitro-2,2'-biquinoline dioxide (0.5 g.) was heated at reflux for 4 hours with a solution which had been previously prepared by dissolving 1 g. of sodium in 40 ml. of absolute methanol. The dark solution, which contained a small amount of solid material, was filtered into 200 ml. of ice water. The slurry of crude 4,4'-dimethoxy-2,2'-biquinoline dioxide was neutralized with dilute hydrochloric acid and dried in a vacuum desiccator. The yield of crude product, melting at 263-265°, was 250 mg. This was then suspended in 25 ml. of chilled chloroform, to which was added 4 ml. of phosphorus trichloride over a 15 minute period. The resulting orange solution was heated at 65-70° for one hour and then quenched with water. The suspension of 4,4'-dimethoxy-2,2'-biquinoline was neutralized with dilute sodium hydroxide and the chloroform was removed by distillation. The crude tan product was separated by filtration, washed with water and dried. The yield of product melting at 237-240° was 0.25 g. (45%). An analytical sample, melting at 250-252°, was prepared by repeated recrystallizations from benzene. *Anal.* Calcd. for $C_{20}H_{18}N_2O_2$: C, 75.93; H, 5.10. Found: C, 75.49; H, 5.45.

(B) From 4-Methoxyquinoline-N-oxide.

4-Methoxyquinoline-N-oxide was prepared by a procedure adapted from Ochiai's (14) method for the preparation of 4-benzyloxyppyridine-N-oxide.

A mixture of 8.5 g. of 4-nitroquinoline-N-oxide and 5 g. of commercial sodium methoxide in 100 ml. of reagent grade absolute methanol was refluxed for 2.5 hours at 68°. The solution of crude product was filtered and evaporated to dryness on a steam bath. The resulting 4-methoxyquinoline-N-oxide, which separated as an oil, was used directly in the catalytic dehydrogenation experiment. The yield was 5 g., and after standing for several weeks, the product crystallized.

One g. of 4-methoxyquinoline-N-oxide was heated with 150 mg. of commercial 5% palladium on carbon in a test tube at 160°. An oil bath was used as the heating medium and the reaction mass was frequently stirred with a thermometer. Heating was continued for 24 hours after which the dark product was suspended in 30 ml. of chloroform to which was added 5 ml. of phosphorus trichloride. This mixture was refluxed for 2 hours at 63°, and the catalyst was removed by filtration. The solution of 4,4'-dimethoxy-2,2'-biquinoline was poured into ice water and the chloroform removed by distillation. The precipitated product was isolated by filtration, washed with water, and dried in a vacuum desiccator. The washings gave a strong test on addition of copper (I) ion. The yield of product melting at 245-250° was 150 mg. (13.5%). A purified sample, prepared by several recrystallizations from benzene, did not depress the melting point of 4,4'-dimethoxy-2,2'-biquinoline which had been prepared from 4,4'-dinitro-2,2'-biquinoline dioxide (m.p. 250-252°). For the purpose of determining whether thermal or catalytic deoxygenation had taken place prior to treatment with phosphorus trichloride, a second catalytic dehydrogenation experiment was run. In this case the reaction mass was not treated with the phosphorus trihalide. A chloroform extract of the dark reaction mixture gave a strong test for cuprous ion, indicating that deoxygenation had probably occurred prior to coupling. Biquinoline dioxides do not give positive tests for cuprous ion.

4,4'-Diethoxy-2,2'-biquinoline.

To a solution of 1 g. of sodium metal in 50 ml. of absolute ethanol was added 0.5 g. of 4,4'-dinitro-2,2'-biquinoline dioxide. The mixture was refluxed for 4 hours and the resulting solution was poured into 200 ml. of ice water. The slurry of crude 4,4'-diethoxy-2,2'-biquinoline dioxide was neutralized with dilute hydrochloric acid. The precipitate was removed by filtration, washed with water, and dried in a vacuum desiccator. The yield of crude product, melting at 257-260°, was 0.2 g. The dioxide was taken up in 25 ml. of chloroform, and 3 ml. of phosphorus trichloride was added. This suspension was heated for 50 minutes at 60° and then poured into ice water. The slurry was neutralized with dilute sodium hydroxide and the chloroform removed by distillation. The precipitated product was isolated by filtration, washed with water and dried. The yield of product melting at 205-210° was 100 mg. (22%). An analytical sample, prepared by several recrystallizations from benzene, melted at 219-221°. *Anal.* Calcd. for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85. Found: C, 76.66; H, 5.87.

4,4'-Dichloro-2,2'-biquinoline. (A) From 4,4'-Dinitro-2,2'-biquinoline Dioxide.

4,4'-Dinitro-2,2'-biquinoline dioxide (0.5 g.) was heated at reflux with 10 ml. of acetyl chloride. During a total heating period of 2 hours an additional 6 ml. of acetyl chloride was added to the solution. Phosphorus trichloride (5 ml.) was then added and heating was continued for 45 minutes at 55°. The solution was poured into 100 ml. of ice water and the suspension neutralized with 20% sodium hydroxide solution. The precipitated 4,4'-dichloro-2,2'-biquinoline was separated by filtration, washed with water and dried in a vacuum desiccator. Repeated crystallizations from benzene yielded 70 mg. of pure product (18%) melting at 306-307°.

Anal. Calcd. for $C_{18}H_{10}Cl_2N_2$: C, 66.48; H, 3.10. Found: C, 66.73; H, 3.18.

(B) From 2,2'-Biquinoline Dioxide.

Four g. of 2,2'-biquinoline dioxide was added over a 15-minute period to 23 ml. of chilled phosphorus oxychloride in a round-bottomed flask equipped with a thermometer and drying tube. The temperature was maintained at 25° or less by means of an ice bath. After the addition of the dioxide the flask was set up for reflux and the temperature was raised to 70°, whereupon a vigorous reaction took place with a rapid rise in temperature accompanied by the evolution of hydrogen chloride. The solution was refluxed for 1 hour at 107° and then poured slowly over 200 g. of ice. After the decomposition of the phosphorus halide, the suspension of crude 4,4'-dichloro-2,2'-biquinoline was neutralized with 20% sodium hydroxide solution. The precipitate was removed by filtration and washed with water and dried. A single recrystallization from dimethylformamide gave 1.1 g. (24%) of essentially pure product melting at 303-305°. A sample of purified 4,4'-dichloro-2,2'-biquinoline, prepared by repeated crystallization from benzene, did not depress the melting point of the dichloro compound which had been prepared from 4,4'-dinitro-2,2'-biquinoline (m.p. 306-307°).

4,4'-Dibromo-2,2'-biquinoline.

To a suspension of 0.6 g. of 4,4'-dinitro-2,2'-biquinoline dioxide in 15 ml. of chloroform was added 8 ml. of phosphorus tribromide. The mixture was refluxed for 0.5 hours, then an additional 2.5 ml. of phosphorus tribromide in 30 ml. of chloroform was added and reflux was continued. After a total heating period of 2.5 hours the solution was poured into 200 ml. of ice water and neutralized with 20% sodium hydroxide solution. The chloroform was removed by distillation and the crude product was isolated by filtration, washed with water, and dried. The crude 4,4'-dibromo-2,2'-biquinoline was repeatedly recrystallized from dimethylformamide. The purified pale yellow product melted at 318-320°, and was obtained in 12% yield (80 mg.).

Anal. Calcd. for $C_{18}H_{10}N_2Br_2$: C, 52.20; H, 2.43; N, 6.77. Found: C, 52.46; H, 2.97; N, 6.77.

4,4'-Dipiperidino-2,2'-biquinoline Dioxide.

To a solution of 15 ml. of piperidine in 10 ml. of dimethylsulfoxide was added 0.6 g. of 4,4'-dichloro-2,2'-biquinoline. The mixture was refluxed for 4 hours at 119° and then poured over 100 g. of ice. The tan crystals were removed by filtration, washed with water, and dried in a vacuum desiccator. The washings gave a strong test, on addition of copper (I) ion. A single crystallization from benzene-hexane yielded 350 mg. (45%) of essentially pure 4,4'-dipiperidino-2,2'-biquinoline melting at 229-233°. An analytical sample was prepared by several crystallizations from a 50:50 benzene-hexane mixture. The product melted at 231-233°.

Anal. Calcd. for $C_{28}H_{30}N_4$: C, 79.58; H, 7.16. Found: C, 79.47; H, 6.90.

4,4'-Dipyrrolidino-2,2'-biquinoline.

A solution of 15 ml. of pyrrolidine in 15 ml. of dimethylsulfoxide was refluxed with 0.6 g. of 4,4'-dichloro-2,2'-biquinoline for 6.5 hours at 110°. The crude product was isolated by pouring the solution into ice water, removing the ensuing precipitate by filtration, washing it with water, and drying the precipitate in a vacuum desiccator. From several crystallizations from benzene the pure product was obtained which melted at 290-292°. The yield of pure 4,4'-dipyrrolidino-2,2'-biquinoline was 80 mg. (11%).

Anal. Calcd. for $C_{28}H_{28}N_4$: C, 79.15; H, 6.64. Found: C, 79.50; H, 6.60.

4,4'-Diphenoxy-2,2'-biquinoline.

One g. of sodium metal was dissolved in 20 ml. of molten phenol and the temperature was raised to 120°, when 30 ml. of dimethylsulfoxide was added to dissolve the precipitated sodium phenoxide. 4,4'-Dichloro-2,2'-biquinoline (0.5 g.) was added and the temper-

ature maintained at 140° for 1 hour. The dark red solution was poured into 200 ml. of ice water and the suspended 4,4'-diphenoxy-2,2'-biquinoline was then removed by filtration. It was washed with water and dried. The pure product was obtained in 19% yield (130 mg.) by repeated crystallizations from benzene. The melting point was 287-288°.

Anal. Calcd. for $C_{30}H_{20}N_2O_2$: C, 81.79; H, 4.56. Found: C, 82.19; H, 4.69.

4,4'-Dihydroxy-2,2'-biquinoline.

4,4'-Dichloro-2,2'-biquinoline (0.6 g.) was dissolved in 100 ml. of 50% (by volume) sulfuric acid. The solution was refluxed for 3 hours at 125°. A small amount of solid material precipitated during the time of reflux. The solution of 4,4'-dihydroxy-2,2'-biquinoline was poured into 200 ml. of ice water, and the dihydroxy compound precipitated. It was removed by filtration, washed free of acid with water, and dried in a vacuum desiccator. The yield was 0.3 g. (54%) of product melting over 360°. The highly insoluble, crude dihydroxy compound was crystallized four times from aqueous dimethylsulfoxide. The purified product had a melting point of over 360°.

Anal. Calcd. for $C_{18}H_{12}N_2O_2$: C, 75.01; H, 4.18. Found: C, 75.00; H, 4.46.

4,4'-Dithiophenoxy-2,2'-biquinoline.

In a 100 ml. round-bottomed flask, 10 ml. of thiophenol was heated at reflux with 0.7 g. of 4,4'-dichloro-2,2'-biquinoline, at 169° for 2 hours. After the heating period the yellow solution was taken up with 150 ml. of absolute ethanol, which precipitated the 4,4'-dithiophenoxy-2,2'-biquinoline. The product was removed by filtration, washed with alcohol, then by water, and dried. Recrystallization from aqueous dimethylformamide gave pale yellow needles of the pure product (m.p. 288-290°). The yield was 0.22 g. (22%).

Anal. Calcd. for $C_{30}H_{20}N_2S_2$: C, 76.23; H, 4.27; N, 5.93. Found: C, 76.51; H, 4.29; N, 6.19.

4,4'-Di(*p*-chlorophenoxy)-2,2'-biquinoline.

To 5 g. of *p*-chlorophenol dissolved in 15 ml. of diethylene glycol dimethyl ether (Diglyme) was added 3 g. of a 50% sodium hydroxide solution. The water was removed by distillation. The solution was then cooled and 1 g. of 4,4'-dichloro-2,2'-biquinoline dissolved in 15 ml. of dimethylformamide was added. The latter was necessary to dissolve the dichloro compound. This solution was refluxed for 2 hours and poured into 200 ml. of ice water. The slurry of crude 4,4'-di(*p*-chlorophenoxy)-2,2'-biquinoline was filtered, washed with water until there was virtually no odor of phenol, and dried. Three recrystallizations from aqueous dimethylformamide gave pale yellow needles of the pure product which melted at 348-350°, in a yield of 20% (330 mg.).

Anal. Calcd. for $C_{30}H_{18}Cl_2N_2O_2$: C, 70.71; H, 3.56. Found: C, 70.37; H, 3.58.

4,4'-Di(*p*-bromophenoxy)-2,2'-biquinoline.

In a 100 ml. round-bottomed flask 6 g. of *p*-bromophenol in 15 ml. of Diglyme was treated with 2.8 g. of 50% sodium hydroxide solution. The water was removed by heating the solution until the temperature reached 165°. The solution was then cooled. 4,4'-Dichloro-2,2'-biquinoline (0.8 g.) was then added together with 15 ml. of dimethylformamide. The solution was refluxed for 2 hours and then poured into 200 ml. of ice water to precipitate the 4,4'-di(*p*-bromophenoxy)-2,2'-biquinoline. The suspended product was removed by filtration, washed free of unreacted phenol with water, and dried. Four crystallizations from aqueous dimethylformamide yielded yellow needles of the pure product (m.p. greater than 360°). The yield was 200 mg. (13.5%).

Anal. Calcd. for $C_{30}H_{18}Br_2N_2O_2$: C, 60.21; H, 3.03. Found: C, 60.20; H, 3.18.

4,4'-Di(*p*-fluorophenoxy)-2,2'-biquinoline.

To 6 g. of *p*-fluorophenol in 15 ml. of Diglyme was added 3.5 g. of 50% sodium hydroxide solution. The water was removed by distillation and the solution cooled. 4,4'-Dichloro-2,2'-biquinoline (0.5 g.) was then added together with 15 ml. of dimethylformamide. The solution was refluxed for 2 hours and then poured into 300 ml. of ice water. The precipitated crude product was removed by filtration, washed free of the phenol and dried. Repeated crystallizations from aqueous dimethylformamide gave 130 mg. (15%) of pure product, melting at 318-320°.

Anal. Calcd. for $C_{30}H_{18}F_2N_2O_2$: C, 75.62; H, 3.81. Found: C, 75.27; H, 3.84.

4,4'-Di(β -naphthoxy)-2,2'-biquinoline.

In a 100 ml. round-bottomed flask 2 g. of β -naphthol and 1.5 g. of 50% sodium hydroxide solution were dissolved in 15 ml. of Diglyme. The water was distilled from the solution, which was then cooled. 4,4'-Dichloro-2,2'-biquinoline (0.4 g.) in 15 ml. of dimethylformamide was added and the solution was refluxed for 1.25 hours when it was poured into 300 ml. of ice water. The slurry was made alkaline with 5 ml. of 50% sodium hydroxide solution and the precipitated 4,4'-di(β -naphthoxy)-2,2'-biquinoline was separated by filtration, washed free of naphthol, and dried. Repeated crystallizations from aqueous dimethylformamide gave 86 mg. of pure product (14%) which melted at 279-281°.

Anal. Calcd. for $C_{38}H_{24}N_2O_2$: C, 84.42; H, 4.47. Found: C, 84.48; H, 4.41.

ULTRA VIOLET STUDIES

Molar extinction coefficients were determined as follows: A 0.00996 *M* solution of cupric ion was prepared by dissolving 2.487 g. of reagent grade copper sulfate pentahydrate in sufficient distilled water to make one liter. The pH was adjusted to three with concentrated sulfuric acid. Ten ml. of this solution was diluted to 100 ml. with distilled water yielding a solution 0.000996 *M* in copper, and containing 0.063 mg. of copper per milliliter of solution.

In a 10 ml. volumetric flask 3-8 mg. of chelating agent was dissolved in 7 ml. of a 5:4 (V/V) solution of reagent grade dimethylformamide: absolute ethanol. A slight excess of hydroxylamine hydrochloride was added as a reductant for the cupric ion. One ml. of the stock copper solution was added by pipette and the solution made up to the mark with the dimethylformamide-ethanol solution. The formation of the characteristic purple color was immediate, and some heat was evolved due to hydration. The solution was cooled to room temperature. It was necessary to employ a 5-10 molar excess of the chelating agent. If a lesser concentration was used it was found that the solutions did not obey Beer's law.

Dilutions for the Beer's law plots were made by pipetting 5 ml. of the above solution and diluting to 10 ml. with a 5:4:1 (V/V) solution of dimethylformamide, absolute ethanol, water. This diluting process was repeated twice and the final copper concentrations are shown in Table II. The wave length of maximum absorption for the respective complexes was obtained and the optical density of the various solutions was then determined at this wave length using a Beckman DU spectrophotometer. The absorptivity was plotted and the straight lines obtained indicate that the solutions follow Beer's law.

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