hemin chloride in dioxane, 643–618, 550–520, 510–495 $m\mu$ was replaced by 604–544, 517– $m\mu$. The thoroughly washed chloroform was dried over anhydrous potassium carbonate, concentrated to 2 cc., and 10 cc. of hot hexane added carefully to the center of the solution. After about five hours, dark-purple crystals began to form on the glass. After a day they were filtered off, washed with hexane, and dried; yield 175 mg. or 72%.

Recrystallization.—Since many halogen-containing solvents, such as chloroform, slowly yield chloride ion through air oxidation, non-halogen solvent was used for the recrystallization. One hundred milligrams of the crude product was dissolved in 10 cc. of hot methanol. The solution was filtered, concentrated to 4 cc., stoppered tightly, and allowed to stand at room temperature. After two hours crystal nuclei began to form on the bottom. After standing in the icebox overnight the crystals were filtered off, washed with 30% aqueous methanol, and vacuum dried. Concentration of the mother liquor to 2 cc. yielded, after cooling twenty-four hours in the icebox, additional crystals of equal size and purity; yield 47 mg. or 47%; m. p. 200–201° (cor.) but varies considerably depending on the manner of heating. The product was glistening macro crystals about 1 × 0.5 × 0.5 mm. purple-black in color with a bluish metallic luster. Spectrum in dioxane, 604–578, 567–532, 513– $m\mu$; rather broad and diffuse.

Method B (Direct preparation from mesoporphyrin dimethyl ester).—Two hundred fifty milligrams of mesoporphyrin dimethyl ester, 400 mg. of C. P. sodium acetate, and 5 cc. of acetic acid were placed in a six-inch test-tube equipped with a mechanical stirrer and heated to 100 by means of a water-bath. A solution of ferrous acetate containing 150 mg. of iron was added drop by drop. The solution was stirred for three-quarters of an hour at 100 and then boiling water added to incipient precipitation (12.5 cc.). The solution was stirred for a half-hour longer and allowed to cool slowly. The purple crystalline product was filtered off, washed with water, and dried in a vacuum desiccator; yield 240 mg. Spectrum in dioxane, 635–620, 604–557, 536– $m\mu$ (a mixture of the hematin and the hemin acetate). The crude product was dissolved in 25 cc. of ethanol, and 0.5 cc. of water added to permit hydrolysis of the acetate. The solution was filtered, concentrated to 10 cc. and allowed to cool. Crystals formed very slowly. After two days a considerable amount of fairly large purple crystals had formed. These were mixed with a small amount of light brown amorphous product. The mixture was shaken, allowed to stand until most of the heavy crystals had settled, and the supernatant liquid containing the amorphous suspension withdrawn with a medicine dropper. The filtered mother liquor was returned to the crystals, and the process repeated until the latter were free of amorphous material. They were finally filtered, washed with 30% methanol and dried; yield 117 mg. or 48.5%; m. p. 196–198.5° (cor.) with decomposition; spectrum in dioxane, 604–579, 566–532, 510– $m\mu$; rather broad and diffuse.

Summary

1. An attempt is made to apply studies on the visible and ultraviolet absorption curves of ferric mesoporphyrin complexes to the interpretation of the chemical structure of these compounds.

2. We conclude that dioxane solutions of the perchlorate, the bisulfate and the pyridine complex of the chloride are both ionized and dissociated.

3. The chloride, bromide and iodide, while ionized are probably not dissociated, the ions being associated so that the absorption curves of the halides differ.

4. The hydroxide, or hematin, differs so much that we must assume a different type of bonding, probably covalent.

5. In the pyridine complex of the hydroxide, it seems necessary to assume the presence of seven covalent bonds to the iron.

BALTIMORE, 18, MARYLAND RECEIVED APRIL 22, 1946

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION]

The Reaction of β-Naphthol, β-Naphthylamine and Formaldehyde. I. 2-Amino-2'-hydroxy-1,1'-dinaphthylmethane

BY RICHARD S. CORLEY AND ELKAN R. BLOUT

The reaction of β-naphthol, β-naphthylamine and formaldehyde[1] yields several interrelated products, culminating in two previously known compounds, the base which will be known in these papers as Morgan's base, after its discoverer,[2] and 1,2,7,8-dibenzacridine (I)[3] which was first isolated by Reed.[4] The present work is divided into three parts, the first dealing with the intermediate product 2-amino-2'-hydroxy-1,1'-dinaphthylmethane (II), the second[5] with the isomeric 1-(2'-naphthylaminomethyl)-2-naphthol (X), and the third[6] with the dibenzacridine bases formed by the reaction at higher temperatures or from the intermediates by cyclization with loss of water followed by aromatization with loss of hydrogen.

In attempts to isolate the unstable 9,10-dihydrodibenzacridine and any intermediates preceding the formation of the cyclized bases, various aromatic hydrocarbons were employed as solvents. Reactions of molecular equivalents of the reactants in boiling xylene and in toluene gave mixtures of the cyclized bases: namely, 9,10-dihydrodibenzacridine, Morgan's base and dibenzacridine.[3] When benzene was used, however, a new compound, shown to be 2-amino-2'-hydroxy-1,1'-dinaphthylmethane (II), was obtained. This compound, denoted hereafter as the dinaphthyl-

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(1) (a) Ullmann and Fetvadjian, *Ber.*, **36**, 1029 (1903); (b) Senier and Austin, *J. Chem. Soc.*, **89**, 1392 (1906).

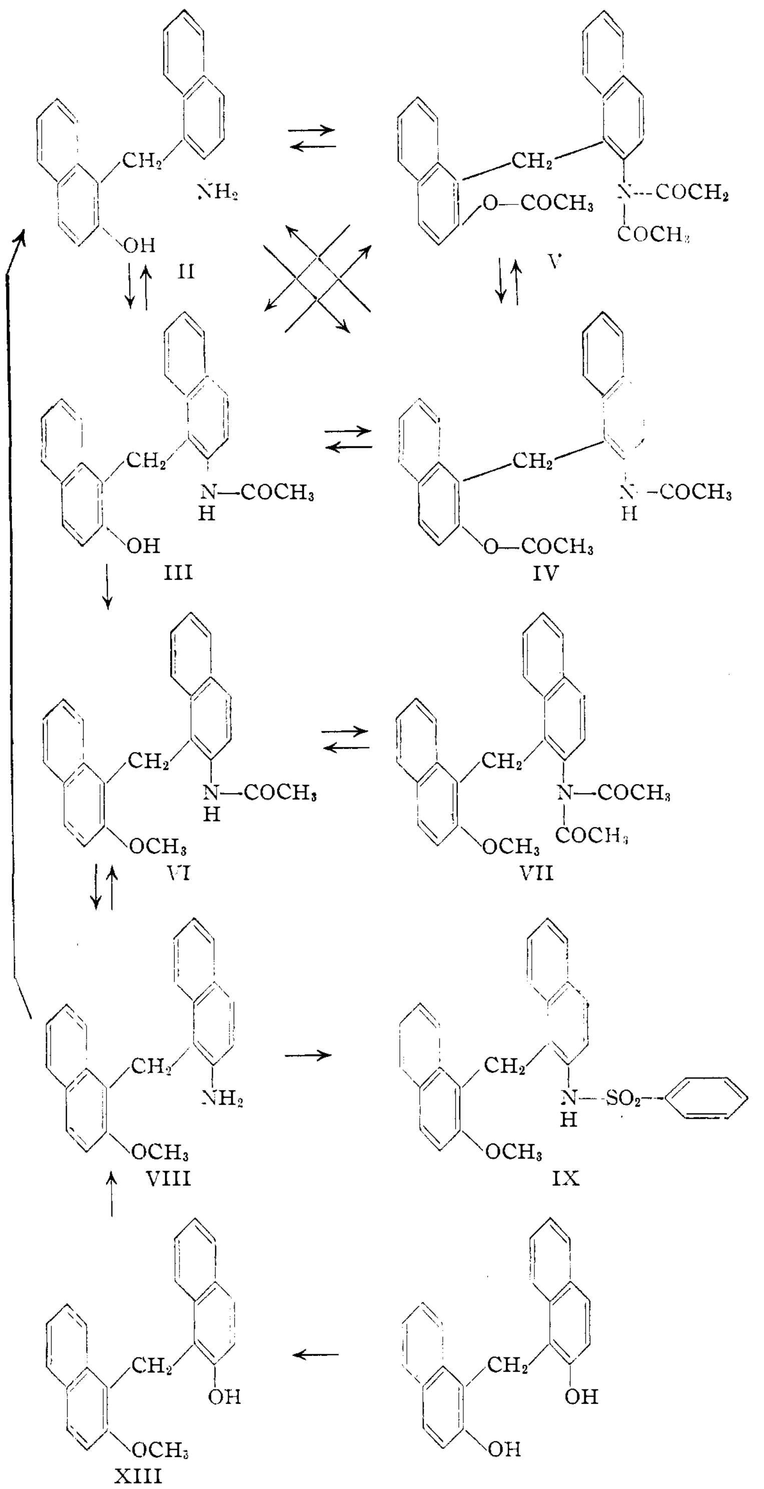
(2) Morgan's "isonaphthacridine," *J. Chem. Soc.*, **73**, 549 (1898), the "naphthacrihydridine" of Möhlau and Haase, *Ber.*, **35**, 4164 (1902), and the "bisdinaphthacridine dihydride" of Senier and Austin.[1b]

(3) Since it is the only dibenzacridine to which reference need be made in this paper, the term dibenzacridine alone will be used to denote 1,2,7,8-dibenzacridine.

(4) Reed, *J. prakt. Chem.*, [2] **35**, 298 (1887).

(5) II, Corley and Blout, THIS JOURNAL, **69**, 761 (1947).

(6) III, Blout and Corley, *ibid.*, **69**, 763 (1947).



methane, decomposes gradually in solution, and rapidly at its melting point with loss of water to form the cyclized bases and other products. Its hydrochloride, on attempted crystallization, decomposed to yield the hydrochlorides of Morgan's base and 1,2,7,8-dibenzacridine. The dinaphthylmethane was characterized by preparation of its N-acetyl (III), N,O-diacetyl (IV), N,N,O-triacetyl (V), N-acetyl-O-methyl (VI), N,N-diacetyl-O-methyl (VII), O-methyl (VIII), and N-benzenesulfonyl-O-methyl (IX) derivatives.

The ready and quantitative formation of the N,N-diacetyl group is presumably due to the presence of a methylene group in the adjacent position, since the presence of an *ortho* methyl group has been found to promote formation of a diacetyl derivative in analogous aniline derivatives.[7] Neither (III), (IV), nor (V) gave a hydrochloride in dry ether or benzene. The secondary N-acetyl substituent and the O-acetyl group are hydrolyzed by alkali in the cold, regenerating (III) which is soluble in alcoholic alkali, with such ease as to confer on (IV) and (V) an apparent solubility in dilute alcoholic alkali.[8] Vigorous hydrolysis of each of the acetyl derivatives gave back the dinaphthylmethane (II). The N-acetyl-O-methyl derivative (VI) was obtained from the N-acetyl derivative (III), and also from the other acetyl derivatives, by methylation with dimethyl sulfate in alcoholic alkali. By refluxing this compound with acetic anhydride the N,N-diacetyl-O-methyl derivative (VII) was obtained. The latter readily lost the secondary acetyl group on solution in alcoholic alkali, regenerating the N-acetyl-O-methyl compound (VI). Alkaline hydrolysis of the latter gave the O-methyl derivative (VIII) which, on attempted diazotization in acetic acid, was demethylated to the dinaphthylmethane (II).

Consideration was given to the possibility that the dinaphthylmethane (II) was the Mannich

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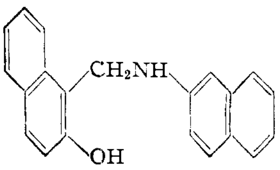
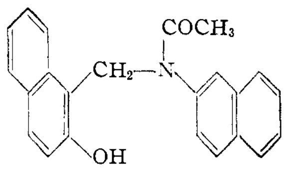
(7) Sudborough, *J. Chem. Soc.*, **79**, 534 (1901); Bistrzycki and Uffers, *Ber.*, **27**, 91 (1894); **31**, 2788 (1898); Uffers and von Janson, *ibid.*, **27**, 93 (1894).

(8) The ease of hydrolysis of phenolic esters is well known [*e. g.*, see Skrabal and Hugetz, *Monatsh.*, **47**, 17 (1926)], but the fact that the secondary amide linkage of such a diacetyl-amine is hydrolyzed by alkali with comparable ease—and much more readily than the primary acetyl group—has apparently received little comment in the literature [Hentschel, *Ber.*, **23**, 2397 (1890)] and is worthy of note. The latter phenomenon has, however, been studied in the case of the N-substituted succinimides. Miolati and Longo, *Atti acad. Lincei*, [5], **3**, I, 597 (1894); Laurent and Gerhardt, *J. prakt. Chem.*, [1], **47**, 71 (1849); Landsberg and Meyer, *Ann.*, **215**, 202 (1882).

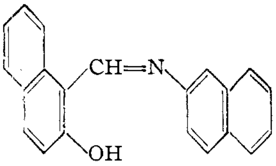
base (X). The Mannich base (X) has a *secondary* amino group, whereas derivatives (V) and (IX) established the presence of a *primary* amino group as required by the dinaphthylmethane formulation (II). Further, the N-acetyl derivative (XI) of the Mannich base was prepared in good yield by reductive acetylation of the Schiff base (XII),[9] obtained by the reaction of 2-hydroxy-1-naphthaldehyde with β-naphthylamine. This acetyl derivative (XI) was not identical with any of the acetyl derivatives of (II); therefore, the structure of the compound cannot be (X).



X



XI



XII

Mayer and Schnecko[10] stated that they obtained the dinaphthylmethane by Bucherer amination of bis-(2-hydroxy-1-naphthyl)-methane, and that it melted at 121°. Since we found the melting point to be 196°, the work of these investigators was repeated several times, but no basic product could be isolated except Morgan's base and dibenzacridine.

Attempts to transform our dinaphthylmethane into the known bis-(2-hydroxy-1-naphthyl)-methane by diazotization and hydrolytic cleavage, as well as similar experiments with the methyl ether, were unsuccessful.

Conclusive proof of the structure of the dinaphthylmethane was obtained by its synthesis from the momomethyl ether of bis-(2-hydroxy-1-naphthyl)-methane (XIII). A Bucherer amination of (XIII) yielded a compound which was found to be identical with the methyl ether of our dinaphthylmethane.

At its melting point the dinaphthylmethane decomposed into two volatile products, water and a molecular compound composed of 1-methyl-2-naphthol and 2-naphthylamine. From the residue there was obtained a molecular compound of dibenzacridine and 1-methyl-2-naphthol, Morgan's base, and a small amount of β-naphthylamine. The 1-methyl-2-naphthol and β-naphthylamine must be formed by reductive cleavage of the methylene–naphthylamine bond, the necessary hydrogen being supplied by the aromatization of the 9,10-dihydrodibenzacridine[6] initially formed by loss of water from the dinaphthylmethane (II).

Ultraviolet Absorption Spectra.—The spectra of β-naphthol and of β-naphthylamine have been redetermined in 95% ethanol and showed general agreement with those previously obtained[11] (Fig. 1). The spectrum of an equimolecular mixture of β-naphthol and β-naphthylamine was determined and found to be nearly identical with the curve calculated from the separate spectra (Fig. 1). Thus, there is only a small degree of interaction between the amine and the phenol at these dilute concentrations (10^{-3} to 10^{-5} *M*). The spectrum of the dinaphthylmethane is given in comparison with that of the equimolecular mixture of β-naphthol and β-naphthylamine and that of bis-(2-hydroxy-1-naphthyl)-methane (Fig. 2). The curve of the dinaphthylmethane is seen to be nearly identical with that of the dinaphthol (effect of the methylene linkage) and that of β-naphthol plus β-naphthylamine (effect of coexistent amino and phenol functions).

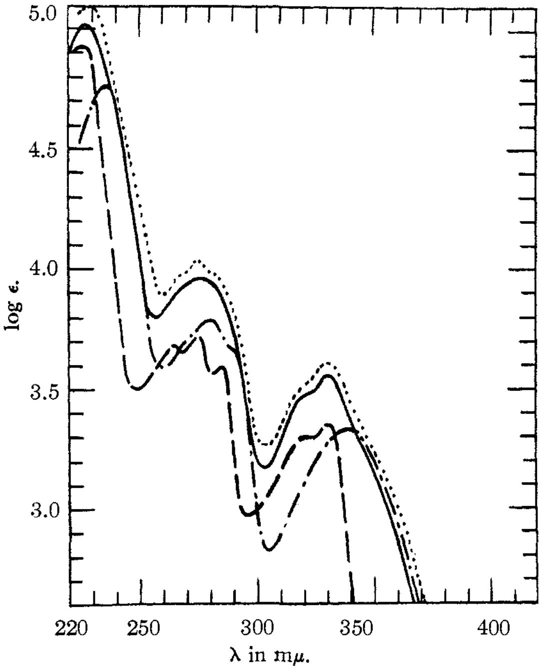


Fig. 1.—(a) — — — — — — — β-Naphthol; (b) — · — · — · — β-naphthylamine; (c)——————1:1 β-naphthol, β-naphthylamine (found curve); (d)·················· 1:1 β-naphthol, β-naphthylamine (calcd. curve).

Experimental

2-Amino-2'-hydroxy-1,1'-dinaphthylmethane (II).—Although the reaction may be carried out on a larger scale, the best and most consistent results were obtained in 10-g. experiments. Ten grams (0.07 mole) each of β-naphthol and of β-naphthylamine (purified by vacuum distillation and crystallization from benzene–hexane), and 2.3 g. of paraformaldehyde (0.071 mole) were boiled for fifteen minutes in 150 cc. of benzene in a flask provided with a

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(9) Bartsch, *Ber.*, **36**, 1975 (1903).

(10) Mayer and Schnecko, *ibid.*, **56**, 1411 (1923).

(11) de Laszlo, *Proc. Roy. Soc.* (London), **111A**, 355 (1926).

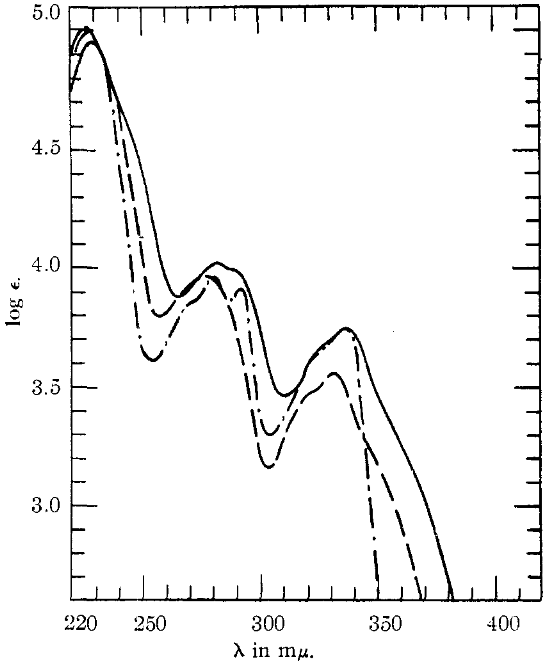

Fig. 2.—(a) ———————— 2-Amino-2'-hydroxy-1,1'-dinaphthylmethane (196° compound); (b) — — — — — 1:1 β-naphthol, β-naphthylamine (found curve); (c) — . — . —.. — bis-(2-hydroxy-1-naphthyl)-methane.

"take-off" reflux condenser. During this time *ca.* 2 cc. of water was removed by azeotropic distillation (removing *ca.* 50 cc. of benzene). The clear brownish-yellow solution deposited on cooling and standing for twelve hours 10.8 g. (52%) of colorless, silky needles of the dinaphthylmethane, m. p. 195–196° (dec.). On further standing, another crop precipitated consisting of nearly pure dinaphthylmethane, which was contaminated with Morgan's base but was usable for the thermal decomposition or preparation of the derivatives. In larger experiments (50 g. of β-naphthol and of β-naphthylamine, 12 g. of paraformaldehyde) mechanical stirring was provided to facilitate boiling and to prevent superheating, and the mixture was boiled for thirty minutes; average yield, 45%.

For analysis the above material was extracted twice by suspension in boiling benzene, collected, washed with hexane, and the colorless, silky needles dried. It melted at 195.5–196.5° (dec. orange melt and evolution of gas).

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.23; H. 5.72; N, 4.68; mol. wt., 299.4. Found:[12] C, 83.91, 83.00; H, 6.47, 5.43; N, 5.31, 4.97; mol. wt. (Rast), 298.

The compound was only very slightly soluble in hot alcohol, ether, benzene, and chloroform; moderately soluble in hot acetone; very slightly soluble in hot dilute aqueous alkali (recovered by neutralization with carbon dioxide); but readily soluble in cold pyridine, hot *n*-butanol, or cold 5% alcoholic alkali (recovered by neutralization). It crystallized from alcohol, ether or benzene, but with contamination by the dibenzacridine bases. It did not couple with benzenediazonium chloride in neutral, acidic or alkaline media.

Hydrochloride.—The hydrochloride was obtained in quantitative yield by leading dry hydrogen chloride into a solution of the base in ether or acetone, colorless leaflets, m. p. *ca.* 205–285° (dec. red-brown melt and evolution of gas).

Thermal Decomposition of the Dinaphthylmethane (II).—Ten grams of the 196° compound was placed in a large "cold-finger" sublimator surrounded by an oil-bath and decomposed by gradually raising the temperature from 195 to 220° in three to four hours. Water-pump vacuum (*ca.* 100 mm.) was applied in order to remove the bulk of the evolved water and obtain a firm cake of sublimate. Sublimate: The brown crystalline material (2.42 g., 24.2%), a molecular compound of 1-methyl-2-naphthol and β-naphthylamine, melted at 133° after several crystallizations from benzene. The constitution of the 133° molecular compound was proved by isolation of 1-methyl-2-naphthol and β-naphthylamine, by treatment with alkali and acid, respectively, which were identified by mixed melting points with authentic samples. For confirmation the molecular compound was prepared by crystallization of a mixture of equimolecular amounts of 1-methyl-2-naphthol (500 mg.) and β-naphthylamine (453 mg.). This procedure yielded 920 mg. (96.5%) of colorless leaflets of the molecular compound, m. p. 131.7–132.6°, and mixed melting point not depressed. The yellow-orange residue (6.90 g., 69.0%) was dissolved in boiling benzene and deposited on cooling 3.50 g. (35%) of Morgan's base in the form of orange needles, m. p. and mixed m. p. 236–246°. The mother liquor was concentrated to 20 cc., 20 cc. of hexane added, and gave on cooling 3.00 g. (30%) of small yellow prisms of the molecular compound of dibenzacridine and 1-methyl-2-naphthol, m. p. 162–170°.[6]

Decomposition of the Dinaphthylmethane Hydrochloride.—One gram of the material, presumably the hydrochloride, which precipitated when an ether solution of II was treated with hydrogen chloride, was taken up in 200 cc. of boiling ethanol. It went into solution slowly to give initially a clear lemon-yellow color, but on further boiling it changed to a dark greenish-yellow, and on cooling deposited a mixture of yellow and dark green needles. After further boiling and concentration of a volume of about 100 cc. the deep blackish-green solution began depositing crystals. On cooling, 0.55 g. of deep green, fine needles of the complex hydrochloride of Morgan's base[6] was obtained. The green hydrochloride, on either heating to 185–200°, or standing for five days in ethanol, gave a good yield of a yellow microcrystalline powder of dibenzacridine hydrochloride,[6] m.p. 346–348° (dec., uncor.). Treatment of the hydrochloride with alcoholic alkali and crystallization from benzene gave light yellow crystals of dibenzacridine, m. p. and mixed m. p. 220°.

N-Acetyl-2-amino-2'-hydroxy-1,1'-dinaphthylmethane (III).—To a solution of 3.00 g. (0.01 mole) of the dinaphthylmethane (II) in 60 cc. of boiling acetone was added 0.95 cc. of acetic anhydride (1.02 g., 0.01 mole) and the solution was concentrated on a steam-bath to a volume of about 20 cc. and 5–10 cc. of ethanol added, whereupon the product began to precipitate; yield 3.29 g. (96.3%). The compound was readily soluble in dilute alcoholic alkali and pyridine, moderately soluble in hot *n*-butanol, and slightly soluble in the usual organic solvents. It did not give a hydrochloride with dry hydrogen chloride in dry ether or benzene. For analysis the compound was crystallized four times from pyridine–water, and twice from butanol to give pure (III), colorless blocks, m. p. 246–248° (slight dec. turning brown). A *labile* dimorphic form (fine needles) was observed several times on crystallization from ethanol.

Anal. Calcd. for $C_{23}H_{19}NO_2$: C, 80.91; H, 5.61; N, 4.10. Found: C, 81.11; H, 5.75; N, 4.55.

Larger amounts of (III) are best prepared by the appropriate number of 5-g. preparations, since some decomposition resulted on larger preparations (25–50 g.) due to the longer time of heating (II) in acetone (probably with formation of Schiff bases and cyclized products) and the reaction gave decreased yields (60–70%). Low solubility made the use of methanol as a solvent awkward, and the use of *n*-butanol resulted in the formation of appreciable quantities of Morgan's base.

Hydrolysis of (III).—Hydrolysis was effected by refluxing a solution of 2.00 g. of (III) in 51 cc. of methanol, 15 cc. of water, and 4 g. of potassium hydroxide for twenty hours. The light-yellow solution did not change in ap-

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[12] All melting points are corrected. Analyses by Dr. Carl Tiedcke.

pearance. It was cooled, diluted with 30 cc. of water and neutralized with solid carbon dioxide. The resulting light-tan precipitate was collected, washed well with water and a little cold ethanol, and dried to give 1.70 g. (97%) of a creamy powder of the dinaphthylmethane (II), m. p. 192–195° (dec.); mixed m. p. 193–196° (dec.). The other alkaline hydrolyses in this paper, except where indicated, were carried out in the same manner. On acid hydrolysis with dilute aqueous-methanolic sulfuric acid the material underwent almost immediate decomposition to give a quantitiative yield of the complex sulfate of Morgan's base, dark, green needles, m. p. 232° (dec.).

N,O-Diacetyl-2-amino-2'-hydroxy-1,1'-dinaphthylmethane (IV).—Ten grams (0.033 mole) of (II) was taken up in pyridine, filtered and washed to give 75 cc. of a slightly brown solution to which 7.0 cc. (0.086 mole) of acetic anhydride was added. After warming for twenty minutes on the steam-bath, the mixture was poured into 400 cc. of cold water with vigorous stirring. One crystallization from pyridine–water gave 12.45 g. (96%) of (IV), m. p. 202–203°. The compound was also prepared by acetylation of (III). The compound was apparently soluble in alcoholic alkali and gave no hydrochloride with dry hydrogen chloride in dry ether or benzene.

For analysis the compound was crystallized three times from pyridine–water, three times from *n*-butanol to give pure (IV), colorless, small cottony needles, m. p. 202.0–202.7°; mixed melting point depressed by both (II) and (III).

Anal. Calcd. for $C_{25}H_{21}NO_3$: C, 78.31; H, 5.52; N, 3.65. Found: C, 78.36; H, 5.70; N, 4.05.

Alkaline Hydrolysis: (a) to (II).—One-half gram of (IV) gave 0.45 g. of a creamy powder of (II), m. p. and mixed m. p. 192–196° (dec.).

(b) to (III).—Seventy-five mg. of (IV) gave on warming only five minutes 70 mg. of a white powder of (III), m. p. 240–244° (slight dec.), and mixed m. p. 246–248° (slight dec.).

N,N,O-Triacetyl-2-amino-2'-hydroxy-1,1'-dinaphthylmethane (V).—Three grams of (II) was refluxed for eighteen hours in 20 cc. of acetic anhydride and *ca.* 3 g. of anhydrous sodium acetate. The light-brown solution was poured into 100 cc. of hot water, and the creamy powder collected and dried to yield 4.18 g. (92%) of (V), m. p. 196–198°. The same compound was also obtained by the acetylation of (III) and (IV).

For analysis the compound was crystallized four times from pyridine–water and once from *n*-butanol to give pure (V), colorless, sparkling, blocky prisms, m. p. 199.0–200.0°, and mixed melting points with (II), (III) and (IV) depressed. The compound was apparently soluble in dilute alcoholic alkali and did not form a hydrochloride.

Anal. Calcd. for $C_{27}H_{23}NO_4$: C, 76.20; H, 5.45. Found: C, 75.95; H, 5.46.

Alkaline Hydrolysis. (a) to (II).—One-half gram of (V) gave 0.35 g. (95%) of a creamy powder of (II), m. p. 184–190° (dec.), and mixed m. p. 188–195° (dec.).

(b) to (III).—Seventy-five mg. of (V) gave on warming only five minutes 70 mg. of a colorless powder of (III), m. p. 240–244° (slight dec.), and mixed m. p. 246–248° (slight dec.).

N-Acetyl-2-amino-2'-methoxy-1,1'-dinaphthylmethane (VI).—Ten grams of (III) (0.0295 mole) was taken up quickly by warming in 150 cc. of methanol and 2 g. of potassium hydroxide, and 7 cc. of freshly distilled dimethyl sulfate (theoretical 3.70 g.) was then added in small portions, adding 10% aqueous sodium hydroxide when necessary to keep the solution basic. After warming ten minutes more on the steam-bath, 50 cc. of water was added and soon a copious white precipitate came out. The mixture was kept warm another ten minutes, then cooled, collected, washed and dried to yield 9.50 g. (91%) of a colorless, crystalline powder of nearly pure (VI), m. p. 214–216°. The compound was also obtained in good yield by the methylation of (IV) and (V) and by the acetylization of (VIII).

For analysis the compound was crystallized four times from pyridine–water and three times from *n*-butanol, to give pure (VI), small colorless, flattened needles, m. p. 217.2–217.5°. It was moderately soluble in hot *n*-butanol, readily soluble in pyridine, difficultly soluble in alcohol and ether, and insoluble in dilute alcoholic alkali. It did not give a hydrochloride in dry ether or benzene. The compound was recovered quantitatively and unchanged after treatment with acetic anhydride in warm pyridine solution.

Anal. Calcd. for $C_{24}H_{21}NO_2$: C, 81.12; H, 5.96; N, 3.94. Found: C, 81.48; H, 6.14; N, 4.11.

N,N-Diacetyl-2-amino-2'-methoxy-1,1'-dinaphthylmethane (VII).—One-half gram of (VI) was refluxed for fifteen hours with acetic anhydride and sodium acetate and worked up according to the method given for the preparation of (V) to give 0.51 g. (91%) of impure (VII), m. p. 178–180.5°, after one crystallization from pyridine–water. For analysis the material was crystallized twice from pyridine–water, three times from *n*-butanol, and dried fifteen hours at 100° (1 mm.) to give pure (VII), colorless prismatic needles, m. p. 178.3–179.3°. It was insoluble in alcoholic alkali and did not yield a hydrochloride.

Anal. Calcd. for $C_{26}H_{23}NO_3$: C, 78.54; H, 5.83. Found: C, 78.94, 78.46; H, 6.11, 6.28.

Hydrolysis of (VII).—Fifty mg. of (VII) was finely powdered, warmed with 8 cc. of 5% methanolic potassium hydroxide, pyridine added until a homogeneous light-yellowish solution was obtained (2–3 cc.), then water immediately added until the solution was saturated. After crystallization, 40 mg. of small prismatic needles of (VI) was collected, m. p. and mixed m. p. 216–217°

2-Amino-2'-methoxy-1,1'-dinaphthylmethane (VIII).—One and one-half grams of (VI) was refluxed for thirty hours in 75 cc. of a 5% solution of potassium hydroxide in *n*-butanol plus 2 cc. of water. On cooling (VIII) separated out as radial clumps of needles which soon filled the flask. This material was collected, washed with a little methanol, then with water, and dried to give 0.80 g. (62%) of needles of (VIII), m. p. 132–134°, which, in marked contrast to (II), is moderately soluble in ether and other common organic solvents.[13] Its solubility in ether may be used to effect a ready separation when necessary from any unhydrolyzed (VI). Hydrolysis in pyridine–water–potassium hydroxide gave a lower yield (25–35%) after separation from unhydrolyzed (VI). For analysis the compound was crystallized four times from ether to give pure (VIII), colorless, silky needles in radial clusters, m. p. 133.6–134.4°.

Anal. Calcd. for $C_{22}H_{19}NO$: C, 84.31; H, 6.11. Found: C, 84.43; H, 6.22.

This gave a hydrochloride on treatment with dry hydrogen chloride in dry ether, which came down initially as a gelatinous semi-solid and changed after a few minutes to small, colorless needles, m. p. *ca.* 230° (dec.), which were converted back to (VIII) by treatment with alcoholic alkali.

Diazotization of 1.50 g. of (VIII) with butyl nitrate and sulfuric acid in glacial acetic acid, followed by decomposition by addition of the mixture to boiling dilute sulfuric acid, gave a brown powder which yielded as the sole phenolic product 50 mg. of the *demethylated* material, (II), m. p. and mixed m. p. 195–196° (dec.). In an attempted Bucherer deamination, 1.50 g. of (VIII) was heated for twenty hours at 150° as a suspension in 35 cc. of 40% sodium bisulfite solution, but gave back 1.42 g. (95%) of unchanged (VIII).

N-Benzenesulfonyl-2-amino-2'-methoxy-1,1'-dinaphthylmethane (IX).—One-half gram of (VIII) was dis-

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[13] The low solubility of (II) in neutral solvents is attributed to the fact that it partakes of a zwitter-ion structure by virtue of the presence within the molecule of both weakly basic and weakly acidic functions. The amino-phenols may be thought of as "semi-zwitter-ions" in comparison with the true zwitter-ions exemplified by the betaines and amino-sulfonic acids.

solved in 5 cc. of pyridine, 0.21 cc. of freshly distilled benzenesulfonyl chloride added (the calculated amount), the orange-brown solution warmed for fifteen minutes on the steam-bath, and then diluted with 20 cc. of water. The resulting thick orange gum was washed by trituration twice with water, twice with dilute hydrochloric acid, again twice with water, and crystallized from acetone–hexane to give 0.43 g. (60%) of colorless, blocky prisms of (IX), m. p. 144–147°. For analysis the compound was crystallized four times from acetone–hexane to give pure (IX), colorless, refractive, thick hexagonal plates (or radial clusters of elongated prisms on more rapid crystallization), m. p. 147.2–148.3°.

Anal. Calcd. for $C_{28}H_{23}NO_3S$: C, 74.15; H, 5.11. Found: C, 74.51; H, 5.31.

It gave with aqueous alkali an insoluble, oily, sodium salt which left a strongly alkaline ash on ignition. It was insoluble in water–methanol but dissolved immediately in the cold upon addition of a few drops of 5% methanolic alkali. Addition of sufficient hydrochloric acid to this solution of the salt gave an immediate precipitate of (IX), m. p. and mixed m. p. 146–147°.

Schiff Base (XII).[9]—To a solution of 5.00 g. (0.029 mole) of 2-hydroxy-1-naphthaldehyde, m. p. 81–82°, in 50 cc. of methanol was added a solution of 4.15 g. (0.029 mole) of purified β-naphthylamine in 25 cc. of methanol plus two drops of 5% alcoholic alkali as a catalyst, and the light orange solution heated on the steam-bath for fifteen minutes. The solution was then seeded and allowed to cool slowly to give 8.55 g. (99%) of bright orange, stubby needles of the Schiff base (XII), m. p. 142–143° (after crystallization from *n*-butanol). Three more crystallizations from butanol gave the pure compound, m. p. 143.5–144.3°.

Anal. Calcd. for $C_{21}H_{15}NO$: C, 84.83; H, 5.09. Found: C, 85.08; H, 5.15.

That the product had the normal aldimine structure was shown by hydrolysis to the parent compounds, 2-hydroxy-1-naphthaldehyde and β-naphthylamine.

1-(N-Acetyl-2′-naphthylaminomethyl)-2-naphthol (XI).—Two grams of the Schiff base (XII), which had been found to be unaffected on standing for twenty hours in contact with acetic anhydride, was dissolved in 45 cc. of glacial acetic acid and 10 cc. of acetic anhydride, and hydrogenated[14] over Adams platinum oxide catalyst at an initial pressure of 45 lb. The brilliant orange color of the solution had changed to nearly colorless, and the calculated amount of hydrogen was taken up in fifteen minutes. Shaking was allowed to continue for another fifteen minutes, the hydrogenation stopped, and the platinum filtered off under suction—not allowing the platinum to become dry, and discarding the washings.[15] The nearly colorless filtrate was evaporated to dryness under carbon dioxide and *in vacuo* at 35–40° and 1 mm., and the residue crystallized from *n*-butanol to give 2.00 g. (87%) of nearly colorless needles of (XI), m. p. 182–183°.

For analysis the product was crystallized four times from butanol to give pure (XI), small colorless needles, m. p. 182.5–182.8°. The m. p. depends on the rate of heating. The value given is for a sample immersed at 180° and heated at a rate of 0.1° per ten seconds.

Anal. Calcd. for $C_{23}H_{19}NO_2$: C, 80.91; H, 5.61. Found: C, 80.63; H, 5.27.

A depression of 8–15° was found on mixed m. p's. of (XI) with each of the three acetyl derivatives of the dinaphthylmethane, (III), (IV) and (V). The compound was soluble in alcoholic alkali and did not form a hydrochloride in dry ether, benzene, or acetone. Its solubility closely approximated that of the N-acetyl derivative (III).

2-Hydroxy-2′-methoxy-1,1′-dinaphthylmethane (XIII).[16]—Fifty grams (0.167 mole) of bis-(2-hydroxy-1-naphthyl)-methane,[17] m. p. 198–200° (dec.), was taken up in 500 cc. of acetone, 10.2 g. (0.183 mole) of potassium hydroxide, 17.3 cc. (0.183 mole) of fresh dimethyl sulfate, and 200 cc. of water added, and the solution refluxed gently for four hours, distilling off 400 cc. of acetone toward the end. The oil which came out solidified in a short time to a nearly colorless, crystalline mass of the crude product, m. p. 128–140°. This was collected, washed with water, and extracted with 400 cc. of 5% sodium hydroxide in 1:1 methanol–water at room temperature. A residue of 5.25 g. (10.5%) of the crude dimethyl ether (XIV), m. p. 140–145°, was filtered off. The product recovered by acidification of the filtrate was crystallized from ethanol to yield 35.05 g. (67%) of colorless, blunt needles of the monomethyl ether (XIII), m. p. 146–148°. Its constitution was proven by its ready methylation to the dimethyl ether, m. p. and mixed m. p. 146–147°, and confirmed by its solubility in alkali.

The product was purified by three crystallizations from ethanol to give the pure compound (XIII), colorless, blunt needles or thin prisms, m. p. 147.2–148.2°.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.03; H, 5.77. Found: C, 83.80; H, 5.81.

Synthesis of 2-Amino-2′-methoxy-1,1′-dinaphthylmethane (VIII).—The finely pulverized monomethyl ether (XIII, 15.0 g.) was suspended in a glass tube with 175 cc. of a freshly made saturated solution of ammonium bisulfite prepared from 230 cc. of concentrated ammonia, 40 g. of sulfur dioxide, and 10 cc. of water. The mixture was then heated at 165° in a sealed tube with continual shaking for seventy-five hours. The crude product, obtained as a light yellow glass from the colorless aqueous solution, was powdered and collected, washing well with water; yield, 14.70 g. The product was dissolved in 400 cc. of dry ether and dry hydrogen chloride led in. The precipitate was collected and washed to give 2.65 g. (16% yield) of the slightly impure hydrochloride of (VIII). Treatment with alcoholic alkali and crystallization from ether gave 1.40 g. of colorless needles of nearly pure (VIII), m. p. 133–134°, and mixed m. p. the same with the product obtained from the dinaphthylmethane. The yield was 9.3% over-all, 72% on the basis of the weight of starting material not recovered. As a check on the identity of the synthetic product, it was acetylated to N-acetyl-2-amino-2′-methoxy-1,1′-dinaphthylmethane (VI), m. p. and mixed m. p. 216–217°.

The filtrate after isolation of the hydrochloride gave on concentration (in three crops) 13.05 g. (87% recovery) of colorless needles of the starting material (XIII), m. p. and mixed m. p. 146–148°.

The absorption spectra measurements were made on a Beckman quartz spectrometer, model DU, using a 1-cm. quartz cell and a hydrogen discharge tube as the ultraviolet source. The solvent used throughout was 95% ethanol.

Summary

The reaction of β-naphthol, β-naphthylamine and formaldehyde in boiling benzene yields 2-amino-2′-hydroxy-1,1′-dinaphthylmethane which is an intermediate in the ultimate formation of the dibenzacridine bases. Its structure is demonstrated by its reactions and by synthesis. On heating to its melting point it decomposes to give the dibenzacridine bases, 1-methyl-2-naphthol and β-naphthylamine.

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(14) For instances of similar hydrogenations, see Buck, THIS JOURNAL, **53**, 2192 (1931).

(15) Our experience in this, and other instances of hydrogenation in glacial acetic acid over Adams catalyst of amino-phenols and similar compounds, has been that if the filtrate is allowed to pass through the *dry* platinum black, it becomes dark brown, and considerable decomposition and reduction of yield is found to have taken place.

(16) *Cf.* Evans and Smiles, *J. Chem. Soc.*, 729 (1937).

(17) Fries and Hübner, *Ber.*, **39**, 440 (1906).