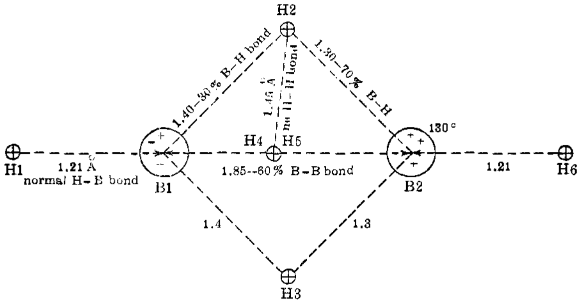


Fig. 3.—A possible four-proton-bridge model for diborane (H4 and H5 lie above and below the plane, and correspond to H2 and H3).

ethane structure in which two protons interact a little more or less than the other four would be easier to reconcile with two strong Raman lines as far apart as 2101 and 2523.[17] One thus visualizes a trigonal antiprism consisting of two sp^2 planar BH_3 groups, held together by B–B and B–H partial cross-linkages, using electrons originally assigned only to the sp^2 orbitals. Such resonance cross-linkage would account for the high barrier against internal rotation[18] quite as would the two-proton bridge, and a slight tipping of one BH_3 prism-face would provide increased or diminished cross-linkage of two protons.

Another method of varying this pseudo-ethane structure would be to slide one triangular face in the direction of the median line from a vertex through the opposite base. Two widely separated protons thus approach each other and four others adjust out of their planes, until the symmetrical two-proton bridge model results. Along the course of this change of models, one finds an infinite number of different possible structures for diborane. Another continuous variable is introduced if one permits the boron atom to depart from the sp^2 plane when cross-linkage first is established, or during the plane-sliding.

Quite as difficult to overthrow as the pseudo-ethane possibilities would be many others involving what might be described as a four-proton bridge. The example shown in Fig. 3 would be consistent with the theory of partial bond orders[19] (roughly extrapolated to orders less than unity), for the total bond order of each proton would be 1.0 and of each boron atom, 3.6. Each boron atom would have a total bonding of 0.6 outside the original BH_3 plane. Such structures, as well as most of the pseudo-ethane types, offer adequate electronic "bareness" on boron to account for the unhindered addition of base molecules.

In view of so many possible and inadequately considered alternatives, it would seem quite inappropriate to accept at this time any specific model as equivalent to the real structure of diborane.

Summary

The H–D exchange reaction between ND_3 and $B_2H_6 \cdot 2NH_3$ reaches equilibrium very rapidly in liquid ND_3 solution at −78°. The extent of exchange corresponds only to the N–H links in $B_2H_6 \cdot 2NH_3$, even at temperatures up to 18°. The reaction between B_2H_6 and ND_3 is not such as to contaminate the excess ND_3 with protons; this is equally true, whether the reaction is carried out at low temperatures (and followed by soaking in liquid ND_3) or at relatively high temperatures, with extensive ammonolysis. Diborane thus fails to yield protons to bases and the borine-complex theory of its base reactions is justified. Possible structural models for diborane are briefly discussed.

Los Angeles, Calif. Received November 9, 1946

---

[17] T. F. Anderson and A. B. Burg, *J. Chem. Phys.*, **6**, 586 (1938).

[18] F. Stitt, *J. Chem. Phys.*, **8**, 981 (1940).

[19] J. E. Lennard-Jones and C. A. Coulson, *Trans. Faraday Soc.*, **35**, 817 (1939).

[Contribution from the Chemical Laboratories of The Johns Hopkins University]

The Nature of the Non-Porphyrin Bonding in Derivatives of Ferriheme[1]

By J. Gordon Erdman[2] and Alsoph H. Corwin

The nature of the bonding in the ferric hemin enzymes such as catalase and the peroxidases requires further study. These enzymes are believed to form, in addition to their protein links, complexes with hydrogen peroxide which are intermediates in the enzymatic processes. In our consideration of the peculiarities of the chemistry of hemoglobin,[1] we have postulated that some, at least, of these phenomena might find an explanation if we assume that globin is bound to ferroheme by two iron to protein links, whereas a single linkage would not permit advancing a geometric argument of the type proposed. If we extend this speculation to the enzymes containing ferriheme, assuming two bonds to the protein, we are faced with the objection that we must assume seven bonds to iron, one more than the usual coordination number of iron. We may refer to the fact that the assumption of the heptavalence of iron in isolated cases is not a new one,[3] and in the

---

[1] Studies in the Pyrrole Series, XIX. Paper XVIII, Corwin and Erdman, This Journal, **68**, 2473 (1946).

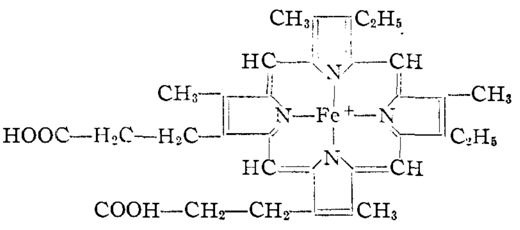
[2] Present address: Mellon Institute, University of Pittsburgh, Pittsburgh, Pennsylvania.

[3] Pauling and Coryell, *Proc. Nat. Acad. Sci.*, **22**, 210 (1936).

case of iron enneacarbonyl it has been supported by X-ray and magnetic data.[4] In the case of the pyridine parahematin of koproporphyrin, Clark and Perkins[5] concluded that their photometric curves on acid–base equilibria of the system were best explained by the assumption of heptavalent iron. Coryell and Stitt[6] also advance this assumption as a possible explanation of some of their data on magnetic susceptibilities. We have submitted the question to an examination by spectroscopic and chemical means and present herewith new evidence that such a valence state may exist in the pyridine complex of hematin.

The most reasonable explanation for a heptavalent state for iron would be that six covalent bonds and one ionic bond were sufficiently similar in energy content to permit their combination into a resonating structure. This is parallel to the suggestion made by Pauling for the structure of phosphorus pentafluoride, in which four covalent bonds and one ionic bond are postulated as being combined in resonance.[7] Our experimental method, in general, has been to subject simple derivatives of ferric mesoporphyrin IX dimethyl ester to spectroscopic examination. Our general conclusions for dioxane solutions are that in the perchlorate and the bisulfate as well as the pyridine complex of the chloride, the acid radicals are both ionized and dissociated. The chloride, bromide and iodide, on the other hand, while ionized are probably not dissociated, the ions being associated in such a manner that the halide ions alter the light absorption of the pigment markedly. The hydroxide, or hematin, differs sufficiently from the other derivatives that we must assume a different type of binding and in the pyridine complex of hematin, whose elementary analysis shows the presence of two molecules of pyridine, the resonating heptavalent structure mentioned above seems the most reasonable one.

The simplest ferric porphyrin entity is the hemin ion. This substance was prepared in solution by



dissolving the hemin hydroxide, or hematin, in either 2% perchloric or 2% sulfuric acid in dioxane. It is assumed that neither the perchlorate nor bisulfate ion has any tendency to associate with the iron. The two curves (Fig. 1, Curves A and B) are similar, being characterized by a weak peak at 615 mμ, a broad low peak at 495 mμ, and a sharp great peak at 390 mμ. The slight discrepancy between the two curves is probably due to traces of halide.

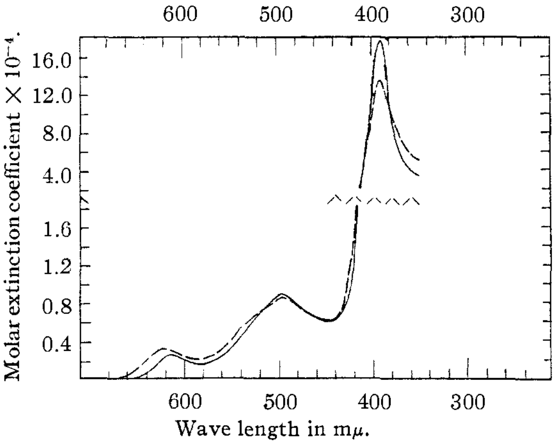


Fig. 1.—Absorption spectra in dioxane: A, ———, ferric mesoporphyrin IX perchlorate; B, - - - -, ferric mesoporphyrin IX bisulfate.

The magnetic data of Pauling and Coryell[8] on solid protohemin IX chloride (natural hemin) indicate that the iron–chloride bond is essentially ionic. We have prepared the entire mesohemin IX dimethyl ester halide series for our studies. Chemically, the iron to halide bonds appear to be ionic. The fluoride shows a strong tendency to decompose into the hematin and hydrogen fluoride. Alcoholic solutions of the other three give the usual precipitates with silver nitrate.

Spectroscopic analysis shows that in dioxane the bond is essentially undissociated. The absorption curves of the chloride, bromide and iodide (Fig. 2, Curves A, B and C) are not identical, nor do their curves coincide with the absorption curve of the hemin ion. The red peak, I, is

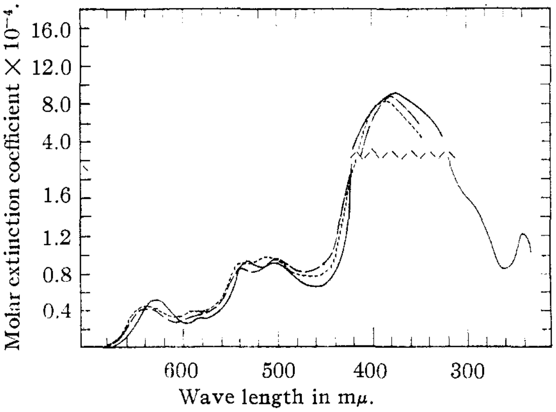


Fig. 2.—Absorption spectra of the halide of ferric mesoporphyrin IX dimethyl ester in dioxane: A, ———, chloride; B, — — —, bromide; C, - - - -, iodide.

---

[4] Powell and Ewens, *J. Chem. Soc.*, 286 (1939). Note that these authors believed $Fe_2(CO)_9$ to contain hexa-covalent iron.

[5] Clark and Perkins, *J. Biol. Chem.*, **135**, 654 (1940).

[6] Coryell and Stitt, THIS JOURNAL, **62**, 2950 (1940).

[7] Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1940, p. 234.

[8] Pauling and Coryell, *Proc. Nat. Acad. Sci.*, **22**, 159 (1936).

shifted toward longer wave lengths, falling at 630 mμ for the chloride, and at 640 mμ for the bromide and iodide. Its intensity is increased in all cases, particularly for the chloride. The band in the green is replaced by a diffuse doublet which shifts slightly to the red as the molecular weight of the halide increases, 500 and 530 mμ for the chloride, 510 and 535 mμ for the bromide, 512 and 535 mμ for the iodide. For the chloride, band II is the most intense, for the bromide and iodide, band III. The great peak is broad and low in all cases, falling at 375 mμ for the chloride, and at 385 mμ for the bromide and iodide. Such changes in spectra probably result from the proximity of the negative halide ion on one side of the ring, the effect varying with the size and consequent closeness of this negative center. The comparisons made above may be criticized because of the change of solvent. The highly ionic acid–dioxane mixtures and pure dioxane are not strictly identical as spectroscopic solvents. The differences between the general halide and the hemin ion curves might be explained away on this ground. Since dioxane is a fairly strong base, the ionic nature of dioxane–hydrogen chloride and dioxane–perchloric acid should be essentially the same. Thus if the above differences are simply due to the change in solvent, the addition of hydrogen chloride to the hemin chloride solution should shift its spectrum toward that obtained for the ion. If, on the other hand, the difference is due to actual association of the hemin and the chloride ions, addition of the latter in the form of hydrogen chloride should have little or no effect on the spectrum. If the hemin chloride is completely associated, hydrogen chloride should have no effect. If it is partially dissociated, hydrogen chloride should shift it still farther away from the spectrum of the ion. The absorption curve for the hemin chloride in dioxane containing 2% dry hydrogen chloride is given in Fig. 3, Curve A. Actually the curve is almost identical with that for hemin chloride in pure dioxane (Fig. 3, Curve B). There seems to be a slight exaltation of peaks I and II relative to III, but this is practically within the assigned error of the measurement. It can therefore be concluded that the hemin halides in dioxane exist almost completely as undissociated ion pairs, the association being intimate enough to cause a marked alteration in the spectrum.

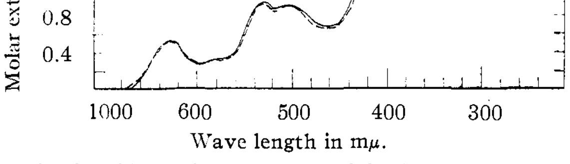


Fig. 3.—Absorption spectrum of ferric mesoporphyrin IX dimethyl ester chloride: A, ———, in dioxane containing 2% of dry hydrogen chloride; B, — — —, in dioxane alone.

Pauling and Coryell[8] interpret the magnetic moment of protohemin IX chloride in pyridine as being due to the presence of five unpaired electrons. This requires that all four internal iron–nitrogen bonds be ionized and that the chloride be ionic as well. The ionic nature of the hemin chloride–pyridine complex is confirmed by the spectrum (Fig. 4, Curve A) which bears a striking resemblance to the curve for hemin ion (Curve C). The whole curve is shifted slightly to longer wave lengths, the red peak falling at 620 mμ, the broad peak at 520 mμ, and the fairly sharp great peak at 395 mμ. The spectrum indicates that the perturbing influence of the chloride ion is no longer present. We interpret this as due to the fact that pyridine is a better complex former than dioxane. Due to its higher dipole moment, it is probably better able to solvate the chloride ion. The latter assumption is borne out by the fact that ammonium chloride is considerably more soluble in pyridine than in dioxane. The net result is separation of the ion pair. Pyridine molecules undoubtedly surround the iron but their influence is symmetrical and too slight to affect the magnetic moment or even the spectrum.

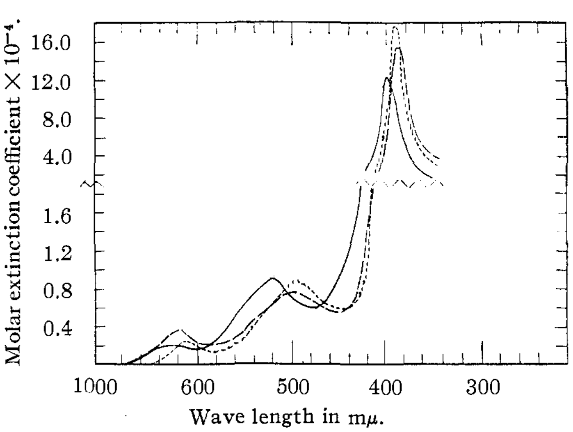


Fig. 4.—Absorption spectra of derivatives of mesohemin IX dimethyl ester: A, ———, chloride in pyridine; B, — — —, chloride in 85% dioxane, 15% tenth molar aqueous perchloric acid; C, - - - -, perchlorate in dioxane.

If the above hypothesis is correct, water should fulfill the same function as pyridine. Qualitative tests with the hand spectroscope indicate that some hydrolysis occurs near the neutral point. The curve (Fig. 4, Curve B) was determined in a mixture of 85% dioxane and 15% tenth molar aqueous perchloric acid, the final

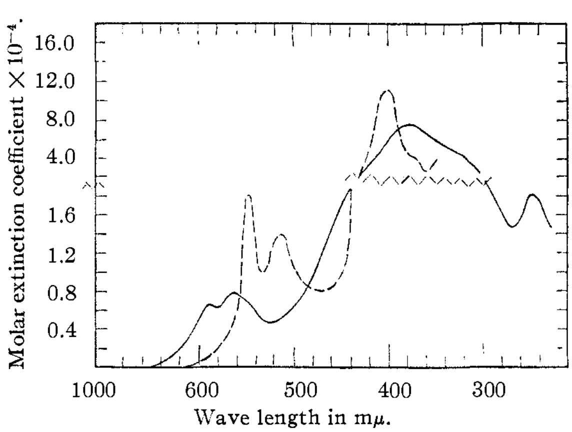


Fig. 5.—Absorption curves of ferric mesoporphyrin IX dimethyl ester hydroxide (mesohematin ester): A, ———, in dioxane; B, — — —, in pyridine.

hydrogen ion concentration being about 2×10^{-2} molar. Further dilution of the dioxane involves the risk of molecular association preliminary to precipitation. The spectrum shows a peak at 620 mμ, with a shoulder on the long wave length side, and a sharp great peak at 390 mμ, thus indicating largely hemin ion, plus a small amount of undissociated chloride. The greater power of water to solvate the chloride ion is slightly outweighed by the combined factors of its dilution with dioxane, and its lesser power of coördinating with iron. The latter is nicely demonstrated by the fact that pyridine is able to displace both water and chloride ion from their respective iron complexes in slightly acid solution.

These results indicate that there is sufficient attraction between the hemin and chloride ions to make it hazardous to rule it out as a possible entity in precise equilibrium studies.

The bonding of the hemin hydroxide, or hematin, is more complicated. Unfortunately the magnetic moment of the neutral molecule has not been determined, either in the solid state or in an inert solvent. Solutions of protohematin-dicarboxylate-ion (hematin in aqueous sodium hydroxide) show a magnetic value in accord with three unpaired electrons. Rawlinson[9] assigns it the square dsp^2 configuration, with covalent bonds to the porphyrin, leaving the iron–hydroxide bond ionic. Since obedience to Curie's law has not been determined in this case, another explanation is possible, namely, that the energy of the octahedral covalent complex, d^2sp^3, of iron, porphyrin, hydroxide, and water is approximately the same as that of the ionic complex, the intermediate moment being due to an equilibrium mixture of the two forms. Only one other case of a possible dsp^2 complex of ferric iron is known, the equally ambiguous basic methemoglobin.[10] The spectrum of hematin (Fig. 5, Curve A) shows a pair of bands at 562 and 588 mμ. The great peak at 380 mμ is broad and low as in the hemin halides. The completely different spectrum proves that free hemin ion and even possibly hemin ion paired with a negative group, the hydroxide ion, are not present in appreciable quantities. The high solubility of the hematin, compared to the hemin halides, in non-polar solvents such as benzene and hexane, indicates a rather non-polar type of linkage.

The stability of the iron–hydroxide bond is further demonstrated when the hematin is dissolved in pyridine. The pyridine does not compete ionically for the position next to the iron. Instead the magnetic moment drops to the value for one unpaired electron, the d^2sp^3 octahedral covalent complex.[9] The spectrum (Fig. 5, Curve B) is also radically different, showing a sharp peak at 548 mμ, a heavy peak at 515 mμ, and a moderately sharp great peak at 400 mμ. The spectrum qualitatively resembles that of the hemochromogens, which also are covalent octahedral d^2sp^3 complexes. The hematin pyridine complex and analogous complexes with other bases, the so-called para-hematins, have been isolated in the crystalline state. In all cases the substances analyze for two molecules of nitrogen base and one hydroxyl per hemin. Heating in vacuum indicates that the base molecules are held firmly and with almost equal strength.[11] Thus to the four porphyrin bonds we must add two for the pyridines and one covalent bond to hydroxide, a total of seven.

The different spectral "genera" among the derivatives of ferriheme have been recognized and classified by workers in the field for decades. Our conclusions, presented above, assume that differences between these genera are caused by differences in bond-type. On this basis the heptavalent state of iron must be considered with respect to the structures of other ferric porphyrin complexes with bases. Additional information is needed before a definite conclusion can be reached as to all details of the bonding in hematin and the parahematins. However, these systems merit still further study for they are probably closely related to the ferric hemin enzymes.

The authors wish to express their indebtedness to the Rockefeller Foundation for a grant which made these studies possible.

Experimental Section

Spectra.—The determinations were made by the method described earlier by Erdman and Corwin.[12] The probable error in wave length is ±2.5 mμ, that in extinction coefficient ±2%.

The Mesohemin Dimethyl Ester Halides.—Ferric ion cannot be put into the porphyrin ring as such. The iron is always introduced in the ferrous state, thus forming the labile ferroporphyrin or heme, which in turn is oxidized by air to the ferric state.

Fluoride.—Two hundred milligrams of mesoporphyrin dimethyl ester and 3 cc. of glacial acetic acid were placed in a six-inch test-tube equipped with a mechanical stirrer

---

[9] Rawlinson, *Australian J. Exptl. Biol. Med. Sci.*, **18**, 185 (1940).

[10] Coryell, Stitt and Pauling, THIS JOURNAL, **59**, 633 (1937).

[11] Fischer, Treibs and Zeile, *Z. physiol. Chem.*, **193**, 156 (1930); Langenbeck, *Ber.*, **65**, 844 (1932).

[12] Erdman and Corwin, THIS JOURNAL, **68**, 1887 (1946).

and heated by means of a water-bath. To the hot mixture was added drop by drop a solution of ferrous acetate, prepared by dissolving 75 mg. of C. P. powdered iron in 3 cc. of 85% acetic acid. After ten minutes, 400 mg. of sodium fluoride was added little by little. The mixture was finally brought to incipient precipitation by the addition of aqueous sodium fluoride. The mixture was allowed to cool and the purple product was filtered off, washed with water and dried; yield 205 mg. or 91.5%.

Recrystallization.—The crude material was dissolved in 3 cc. of absolute methanol and filtered by suction. To the hot filtrate was added one drop of perchloric acid and 3 cc. of hot saturated solution of ammonium fluoride in methanol. On cooling a semicrystalline purple powder separated, which was filtered, washed with methanol, and dried; yield 60 mg. or 29%: spectrum in methanol I, 640-610 mμ; II, 590-550 mμ. The spectrum gradually becomes more diffuse, absorption building up in the region 550-500 mμ, thus indicating hydrolysis to hematin.

Chloride.—Five hundred milligrams of mesoporphyrin dimethyl ester, 100 mg. of finely powdered sodium chloride, and 5 cc. of glacial acetic acid were placed in a six-inch test-tube equipped with a mechanical stirrer. The tube was left open to the air. As soon as the porphyrin had completely dissolved a hot solution of ferrous acetate, containing 150 mg. of iron, was added drop by drop. The solution turned brown and the mesohemin dimethyl ester chloride began to separate. It was stirred vigorously for ten minutes to complete the oxidation. After cooling to room temperature, the dark purple crystalline solid was filtered by suction, washed with 10 cc. of 30% acetic acid, distilled water until the filtrate was chloride free, 0.5 cc. of methanol and finally 2 cc. of ether; yield 545 mg. or 95%, m. p. 234-244 (cor.) with decomposition.

Recrystallization. Method A.—Two hundred milligrams of the crude product was dissolved in 1.5 cc. of chloroform, filtered by suction and approximately 3 cc. of hot carbon tetrachloride added carefully to the center of the solution to avoid crystallization. When this occurred on the hot-plate violent bumping resulted. The flask was stoppered and cooled slowly to ice-salt temperature. The crystals were filtered off, washed with carbon tetrachloride and vacuum dried; yield 195 mg. or 78%, m. p. 244.3-246.8 (cor.) with decomposition.

Second Recrystallization.—Yield 148 mg. of 76%, m. p. 243.5-245 (cor.) with decomposition. Magnified 125 ×, the pure product appeared as well formed massive plate-like crystals, with oblique extinction. By transmitted light they were amber, by reflected light, metallic purple.

Method B.—Two hundred fifty milligrams of the crude product was dissolved in 2 cc. of pyridine and filtered by suction. The filtrate was added drop by drop to a stirred solution of 5 cc. of glacial acetic acid and 100 mg. of finely powdered sodium chloride. The mixture was heated for five minutes, and 5 cc. of a saturated aqueous sodium chloride solution added drop by drop. Heating was continued for ten minutes and the solution cooled very slowly to ice-salt temperature. The mesohemin dimethyl ester chloride separated in clusters of glistening purple crystals. These were filtered off, washed with 30% acetic acid, water until halogen free, a few drops of methanol and finally 1 cc. of ether; yield 233 mg. or 93%,[13] m. p. 244.5-245.5° (cor.) with decomposition. Magnified 125 ×, the product resembled that obtained by method A.

Bromide.—The mesohemin dimethyl ester bromide was prepared by a method identical with that used for the chloride, except that C. P. sodium bromide was substituted for the sodium chloride; yield 545 mg. or 89%, m. p. 217.5-218 (cor.) with decomposition.

Recrystallization. Method A.—The product was dissolved in 6 cc. of ethylene bromide, filtered by suction, concentrated to 3.5 cc., and hexane added very slowly, drop by drop, until the first crystals began to form. It was cooled slowly to ice-salt temperature, filtered, washed with hexane, and dried; yield 463 mg. or 85%, m. p. 214-216 (cor.) with decomposition.

Second Recrystallization.—Yield 357 mg. or 77%, m. p. 214.5-215.5 (cor.) with decomposition. Magnified 125 ×, the product appeared as purple almost cubical crystals with sparkling facets.

Anal. Sample I. Dried in an Abderhalden pistol for one hour at 1 mm. over methanol. Sample II. Dried two hours over xylene, b. p. 140°.

	C, %	H, %
Found I	53.67	5.23
	53.67	5.21
II	54.18	5.28
Calcd.	59.33	5.54
$+{}^1/_2C_2H_4Br_2$	54.01	5.18
$+1C_2H_4Br_2$	49.67	4.84

The product thus contains a half mole of ethylene bromide as solvent of crystallization. It is probable that in the crystal lattice each iron is surrounded by two bromine atoms, one of which is contributed by the ethylene bromide.

Method B.—Two hundred fifty milligrams of mesohemin bromide one-half ethylene bromide was recrystallized from pyridine-acetic acid. The procedure was the same as for the chloride except that sodium bromide was substituted for the sodium chloride; yield 125 mg. or 56.3%, m. p. 220-222° (cor.) with decomposition. Magnified 125 ×, the product appeared as purple-black rod-like needles tending to grow in rosets.

Anal. Calcd.: C, 59.33; H, 5.54. Found: C, 59.39; H, 5.50.

Iodide.—The mesohemin dimethyl ester iodide was prepared by a method identical with that used for the chloride, except that C. P. sodium iodide was substituted for the sodium chloride. Long standing was avoided as iodide ion in acetic acid slowly oxidizes to iodine. The product was a mat of fluffy purple-red needles, markedly different in appearance from the heavy chloride or bromide; yield 625 mg. or 96%, m. p. 232-234° (cor.) with decomposition.

Recrystallization. Method A.—Two hundred fifty milligrams of the crude material was recrystallized from water-white ethyl iodide and hexane by the same method used for the bromide, Method A; yield 240 mg. or 96%, m. p. 236-238° (cor.) with decomposition.

Second Recrystallization.—Yield 223 mg. or 93%, m. p. 236.5-237.5 (cor.) with decomposition. Magnified 125 ×, the product appeared as rod-like crystals with blunt ends, tending to grow in clusters. The rods were occasionally branched.

Method B.—Two hundred fifty milligrams of the crude material was recrystallized from pyridine-acetic acid. The procedure was the same as for the chloride except that sodium iodide was substituted for the sodium chloride; yield 202 mg. or 81%, m. p. 233-235° (cor.) with decomposition. Magnified 125 ×, the product appeared as long thread-like needles of a reddish-amber color and oblique extinction.

Anal. Calcd.: C, 55.73; H, 5.20; Fe (as ash), 7.20. Found: C, 55.82; H, 5.31; Fe (as ash), 7.19.

Mesohematin Dimethyl Ester.—In addition to the usual purification, all the solvents employed in this section, with the exception of the chloroform, were shaken for two hours with finely powdered silver nitrate and fractionated. Method A. (Modification of the procedure outlined by Fischer, Hummel and Treibs[14] for the preparation of protohematin dimethyl ester.) Two hundred fifty milligrams of mesohemin chloride was dissolved in 150 cc. of chloroform, 1 cc. of 10% C. P. sodium hydroxide added, and the mixture beaten into an emulsion under nitrogen. Twenty-five cubic centimeters of water was added, the mixture shaken, allowed to separate in a pear funnel, and the chloroform layer washed with 50 cc. of water. One cubic centimeter of 10% sodium hydroxide was added and the process repeated twice more. The spectrum of the

---

(13) Fischer and Stangler, *Ann.*, **459**, 73 (1927), quote 246°.

(14) Fischer, Hummel and Treibs, *Ann.*, **471**, 272 (1929).

hemin chloride in dioxane, 643–618, 550–520, 510–495 mμ was replaced by 604–544, 517– mμ. 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– mμ; 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– mμ (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– mμ; 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-

---

[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).