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THE PORPHYRIN-LIKE PRODUCTS OF THE REACTION OF PYRROLE WITH BENZALDEHYDE¹

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Following the verification (5, 6) of Küster's general conception of the porphyrin ring, chemists have sought for the two isomers:



Rothemund (12) announced the separation of porphine into two isomers and later (13, 14) extended the porphyrin isomers to embrace various meso-² (methine-C) substituted compounds, including the tetraphenylporphyrins. In the latter cases, however, the actual isolation and analysis of the several forms has not been reported. The existence of the isomerism is inferred from differences in absorption spectra and acidity. The representation of these forms as isomers of the type of I and II is open to numerous objections and it was the purpose of the present research actually to isolate and establish the nature of the various forms.

The yields of porphine from pyrrole and formaldehyde are so poor that an investigation is extremely tedious. On the contrary, the yields of tetraphenylporphine are sufficiently large to permit of a relatively large source of material. The latter compound was therefore chosen for investigation.

Preparation of material. In a bomb tube of ca. 40 cc. capacity were mixed 5 cc. of redistilled pyrrole, 10 cc. of pyridine,³ and 10 cc. of benzaldehyde. Nitrogen was bubbled through the solution for one-half hour to remove the oxygen and the tubes were sealed. The bombs were placed in a pipe jacket which was in turn suspended in a larger Pyrex tube containing a high-boiling liquid, whose b.p. determined the temperature of the bath. Temperatures tested included 100°, 165°, 190°, 220°, and 245°. The time for which experiments were run varied from five days at the first temperature to eighteen hours at the last. Optimum yields (ca. 10% on the basis of pyrrole) were obtained in 48 hours at 190-220°. Filtra-

¹ Abstracted from the thesis submitted by S. Aronoff in partial fulfillment of the degree of Doctor of Philosophy, May, 1942.

² The implications of the term "meso" used in this connection have no relation to its use for the vinyl-hydrogenated chlorophyll derivatives.

³ Although pyridine was used as solvent in most preparations, the substitution of pyridine by quinoline did not alter the product. These bases therefore do not enter into the structure of the end-products.

tion of the tube contents resulted in purple crystals with properties very similar to those described by Rothemund except for the variable height of band 1 in the absorption spectrum. The products obtained at different temperatures were analytically identical and corresponded to $C_{44}H_{30}N_4$.

For analysis, material was twice recrystallized from benzene with the following results: Anal. Calc'd for $C_{44}H_{30}N_4$: C, 85.96; H, 4.92; N. 9.12.

Found: (for prep'n at 245°) C, 86.10, 85.99; H, 4.74, 4.73; N, 9.29, 9.46.

(for prep'n at 220°) C, 85.75, 85.80; H, 4.75, 4.81; N, 9.24, 9.33.

(for prep'n at 190°) C, 85.7, 85.6; H, 4.94, 4.89;

(190°, quinoline) C, 85.7, 85.6; H, 4.95, 4.92.

Spectroscopically they ranged from types $4,3,2,1^4$ (at 100° and 165°) to 1,4,3,2 (at higher temperatures). It was therefore certain that at least two substances were being formed.

The crystals obtained from the original reaction mixture were further separated into components by chromatographic adsorption on talc using trichloroethylene as solvent. At least six zones appear in the chromatogram (Plate 1) four of which could be separated mechanically. These were eluted with pyridine and the eluate transferred to benzene. The latter was washed with water, dried with sodium sulfate, and concentrated, resulting in crystals of the separate components. Rechromatogrammed individually, these gave only single bands. The spectra of the various components are shown in Figs. 1 and 2. The ratio of the yields of components A:B: (C + D + E + F) is about 10:4:1. It is obvious that the first published (1) curve for "ms-tetraphenylporphine" is the result of low temperature preparation, being almost pure component A (see Table I). The second published (2) curve contains considerable quantities of the other components also show different crystalline structure when rapidly crystallized from methyl iodide (no quaternary nitrogen formed!) (See Plate 2).

Only components A and B were obtained separately in amounts sufficient to permit the determination of properties in addition to the absorption spectrum. The results are summarized in Table I.

Absorption spectra. The differences between the components are shown in their absorption spectra in the visible region. Rothemund has proposed H isomerism primarily on the similarity of the form of the absorption spectra, the essential difference between the isomers being a shift of all the bands of one of the compounds with respect to those of the other.

Isomeric fractions A and B (see Fig. 1) show, however, relatively small shifts in band positions but extreme variations in intensity of the first band. We are not aware of any true porphyrin which shows a 1,4,3,2 spectral type, as does fraction B. Type 4,3,2,1 on the contrary, as shown by fraction A, is similar to that shown by all etioporphyrins and other porphyrins with non-chromophoric β -substitutions (except porphine, which, as noted in the discussion, may itself be a mixture).

The spectra of the other fractions are intermediate between these two extremes. Most interesting is fraction F, in which the narrowness of the bands, characteristic of true porphyrins, is beginning to be lost.

⁴ In this paper verbal nomenclature of porphyrin spectral types will be replaced by numerical, as follows. The bands are numbered 1,2,3,4, on the basis of increasing frequency. Band types are then denoted by arranging band numbers in order of decreasing absorption coefficient. Thus:

"Etio" type, 4,3,2,1

"Rhodo" type, 3,4,2,1

"Chloro" type, 4,2,3,1

Experimental. Absorption spectra were measured in the usual manner with benzene as solvent. Two instruments were used, the Beckman photoelectric spectrophotometer, and the visual Bausch and Lomb Universal spectrophotometer. The spectra obtained checked closely both in positions and height of the maxima and minima.

Acid numbers. These were determined by extraction of ether solutions with aqueous HCl. The acid number is defined as the per cent of acid to extract two-thirds of the pig-



PLATE 1 MIXTURE CHROMATOGRAMMED ON TALC WITH TRICHLOROETHYLENE Components as indicated

ment from ether (equal volumes of acid and ether). The results indicate, inasmuch as the hydrochloride of A is less soluble than B, that component B is a weaker base than component A. As a result of the spectroscopic titration it was found that the first acid dissociation constant of the disalt of B was greater than that of A. Since the monosalt of A exists over such a short range the acid number appears to be determined by the second acid dissociation constant of the salt, which is greater for A than for B.

Both components show reversible dissociation on heating their glacial acetic acid solutions, *i.e.*, when cool, the solution has an acid spectrum, when hot, a free base spectrum.



Components as indicated. Bands at 4000 Å not shown

Hydrochlorides. In contrast to Rothemund's results the hydrochlorides, prepared in the following manner, of the mixture were found to approach a disalt more closely than either a tri- or tetra- salt. The hydrochlorides of the original mixture were prepared by permitting the HCl extract of the ether solutions to stand a few days, at the end of which the salts had

completely precipitated, leaving a colorless aqueous acid solution. (The use of $CHCl_s$ and dry HCl gas as a means of hydrochloride preparation was avoided, since that solvent occasionally tends to add Cl to the molecule, aside from invalidating the analysis itself.)



FIG. 2. FREE BASES

Components as indicated. Bands at 4000 Å not shown. Transmission plotted as $\log 1/T$ in a 1 cm. cell, since absolute concentration not known. Plotted for approximate equivalence at band 2.

The precipitate was washed until virtually acid-free, dried at 100° in vacuo (no dissociation occurred), and then analyzed.

Anal. Cale'd for P·HCl: C, 81.2; H, 4.61; Cl, 5.44. for P·2HCl: C, 76.9; H, 4.40; Cl, 10.3. for P·3HCl: C, 73.0; H, 4.18; Cl, 14.7.

Found: C, 74.8, 75.0; H, 4.61, 4.57; Cl, 8.12, 7.88.

The analysis for chlorine was done by the alkalimetric titration method, and is known to be giving low values.

On heating the hydrochlorides at atmospheric pressure, the HCl dissociates from the molecules and the original porphyrin is regenerated. The hydrochlorides of components A and B were separately prepared and then reconverted into the free base by heat. In each case the original free base was regenerated, as recognized by its absorption spectrum.

TABLE I							
PROPERTIES	of Comp	ONENTS	Α	AND	в		

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PROPERTY	COMPONENT A	COMPONENT B		
Spectral Type (free base) Acid Number Salt	4,3,2,1 13.5 (a) Hydrochloride extremely insoluble in H ₂ O (b) Regenerates original porphyrin on heating	 1,4,3,2 19.5 (a) Hydrochloride somewhat soluble in H₂O (b) Regenerates original porphyrin on heating 		
	(c) $K_2 = 10^{-2}; K_1 = 10^{-2}$ (d) $P \cdot xH_2SO_4$ stable in conc'd H_2SO_4	 (c) K₂ ≥ 10⁻⁵; K₁ ≥ 10⁻¹ (d) P·xH₂SO₄ less stable in conc'd H₂SO₄ 		
Cu Salts	1 band; 5400 Å	2 bands; 6150, 5400 Å		
Solubility (in EtOH)	ca. 3×10^{-5} M/l	ca. 6 \times 10 ⁻⁴ M/l		
Crystal forms (from CH ₃ I)	prisms; twinned at ca. 110°	octahedral		
Temp. of formation	lower temp. required	higher temp. required		
mum condition)	cu, 01%	cu. 21 70		





Dotted line indicates possible resolution of new band in conc'd sulfuric acid

Polyacid basicity. In addition to the spectrum of the free base of component A in an inert solvent, a different spectrum appears in dilute sulfuric acid or concentrated hydrochloric acid (see Fig. 3), and still a different one in concen-

trated sulfuric acid. Dilution of the conc'd acid solution results in reappearance of the dilute acid spectrum. Since these differences are far too great to be accounted for as mere physical effects of changing solvent, on this basis the com-



FIG. 4. COMPONENT A (FREE BASE) + VARYING AMOUNTS OF ALCOHOLIC HCl Initial conc'n of free base identical in all cases (= 3×10^{-3} M/1.) (1) Free base (5 cc. dil. to 10 cc. with alc.); (2) free base (5 cc.) + 0.50 cc. 0.0204 N HCl sol'n dil. to 10 cc.; (3) free base (5 cc.) + 1.00 cc. 0.0204 N HCl sol'n dil. to 10 cc.; (4) free base (5 cc.) + 2.00 cc. 0.0204 N HCl, sol'n dil. to 10 cc.; (5) free base (5. cc.) + 3.50 cc. 0.0204 N HCl sol'n dil. to 10 cc.; (6) free base (5 cc.) + 5.00 cc. 6.3 N HCl sol'n. Taken in 1 cm. cell.

pound must have at least two basic centers. However, as the analysis of the hydrochloride showed two HCl per molecule, and there is a third salt formed in concentrated sulfuric acid, it must have at least three basic centers. The ab-



FIG. 5. COMPONENT B (FREE BASE) + VARYING AMOUNTS OF ALCOHOLIC HCl

Initial conc'n of free base identical in all cases (= 6×10^{-4} M/1.) (1) Free base (2 cc. dil. to 10 cc. with alc.; (2) free base (2 cc.) + 0.25 cc. 0.0204 N HCl sol'n dil. to 10 cc.; (3) free base (2 cc.) + 0.50 cc. 0.0204 N HCl sol'n dil. to 10 cc.; (4) free base (2 cc.) + 5.00 cc. 0.0815 N HCl sol'n dil. to 10 cc.; (5) free base (2 cc.) + 3.00 cc. 6.3 N HCl sol'n dil. to 10 cc.; (6) free base (2 cc.) + 5.00 cc. conc. N HCl sol'n (aq.) dil. to 10 cc. (These six curves were chosen from eleven obtained. Additional curves were omitted for the sake of clarity.) Taken in 1 cm. cell.

sence of an intermediate spectrum between the free base and the disalt shows that the first dissociation constant⁵ (K_2) lies very near the second ($K_1 = 10^{-2}$)

⁵ The discussion of dissociation constants does not include that of the sulfuric acid salt \rightarrow disalt. The first dissociation constant (K_2) is disalt \rightarrow monosalt.

(See Fig. 4) and cannot be estimated separately. Component B shows, in addition to the three spectra corresponding to those just mentioned of component A, a new spectrum at very low acid concentrations (see Fig. 5). It has therefore at least three basic centers. The presence of a different salt formed at low concentration is obvious from the drop in log 1/T at 6500 Å and the increase at 5900 Å. (T is the % transmission). Qualitatively, the intermediate form of a component B has a spectrum consisting of at least a single band with a maximum near 5800 Å. The spectrum may be evaluated quantitatively as follows.

Let the concentration of the free base, $A = u_0$, monosalt, $AH^+ = u_1$, disalt, $AH^{++} = u_2$, so that the acid dissociation constants, K_2 and K_1 may be defined as

1.
$$K_2 = \frac{u_0 x}{u_1}; \quad K_1 = \frac{u_1 x}{u_2}$$

We know that at any x (hydrogen ion concentration)

2.
$$\log \frac{1}{T} = k_0 u_0 d + k_1 u_1 d + k_2 u_2 d$$

where k_0 , k_1 , k_2 are the corresponding molar extinction coefficients and d is the thickness of the absorption cell.

3.
$$u_0 + u_1 + u_2 = c$$

where c is the total concentration of the porphyrin. It has been shown by Hill $(9)^6$ that the concentrations of the ions and undissociated fraction may be expressed by the relations

4.
$$u_0 = \frac{\frac{c}{x^2}K_1K_2}{1 + \frac{K_1}{x} + \frac{K_1K_2}{x^2}};$$
 $u_1 = \frac{\frac{c}{x}K_1}{1 + \frac{K_1}{x} + \frac{K_1K_2}{x^2}};$ $u_2 = \frac{c}{1 + \frac{K_1}{x}\frac{K_1K_2}{x^2}}$

By using the proper combination of the above four equations the following relationship is obtained.

$$\left(\frac{k_0}{x^2} - \frac{\log\frac{1}{T}}{cx^2}\right)K_2 + \left(\frac{1}{x}\right)k_1 + \left(k_2 - \frac{\log\frac{1}{T}}{c}\right)\frac{1}{K_1} = \frac{\log\frac{1}{T}}{cx}$$

Thus by selecting, at some particular wave length, three values of $\log 1/T$ and the corresponding values of x it is possible to solve the resulting set of three simultaneous equations for the unknowns k_1 , K_1 , K_2 , since k_0 , x, and c are known and k_2 can be taken from the spectrum in the most concentrated acid solution.

A complete solution of the curve demands a set of simultaneous equations at every point. A minimum solution demands only a single set from which u_0 and u_2 are obtained. Knowing the values of k_2 and k_0 the curve corresponding

⁶ A joint paper by one of us (S. A.) with this author dealing with the general application of equilibria in polycomponent spectroscopic systems will be published shortly.

to their sum is erected and the curve corresponding to u_1 is obtained by subtraction of the erected curve from the experimental one at the chosen x (see Fig. 6).

In the actual experiment, the pure components were dissolved in ethanol and titrated with known concentrations of dry hydrogen chloride (see Figs. 4 and 5). Using the data at four wave lengths, we obtained the results of Table II.



FIG. 6. CONTRIBUTION OF DISALT TO OBSERVED SPECTRUM •, Observed spectrum. Solid line, monosalt spectrum obtained by subtraction

The absorption coefficients calculated independently (Table II) fall on the spectrum obtained by subtraction (points designated by x).

Cu complex. Most Cu-porphyrins show an absorption spectrum containing two primary bands in positions similar to that of the Cu salt of B (see Fig. 7). Fraction A has only one primary, its position being identical with the corresponding band of component B. The published data (2) show the influence of Cu-B in the spectrum of Cu-A.

TABLE II

	K_2^{a}	$K_1{}^a$	$k_1(\times 10^{-4})$
650	0.91×10^{-4}	3.63×10^{-2}	1.75
630	0.14×10^{-4}	$5.25 imes 10^{-2}$	1.70
610	0.09×10^{-4}	0.13×10^{-2}	1.29
590	$4.64 imes 10^{-4}$	114×10^{-2}	1.71
Geometric mean	$2.3~ imes~10^{-5}$	1.7×10^{-1}	

^a Expressed as basic dissociation constants the first one becomes 10^{-9} and the second 10^{-13} . The spread in the values is to be interpreted in the nature of the curves, not the method of calculation.



FIG. 7. Cu-COMPLEX Components as indicated

These complexes are, like those of the porphyrins, stable in concentrated sulfuric acid, and boiling in the solvent does not remove the metal.

The complexes were prepared in the usual manner: 5 mg. of the porphyrin was heated to boiling in 1 cc. of glacial acetic acid. Fifty milligrams of copper acetate and 150 mg. of



PLATE 2 (a) Component A; (b) Component B; (c) Components C + D

sodium acetate were added, and the mixture boiled 2-3 minutes. After cooling, 25 cc. of ether and 50 cc. of water were added and the mixture shaken. The ether layer, containing the Cu-complex, was washed 2-3 times with water and then with 25% hydrochloric acid until free of unreacted free base (*i.e.*, until the acid washes were colorless). The ether was

then washed again, dried, and concentrated, resulting in beautiful orange crystals of component A and purple crystals of component B.

Crystal form. Still additional differences of the fractions are found in their crystal forms (Plate 2). Fraction A crystallizes in twinned prisms, the twinning angles being ca. 110°. The tendency to multiple twinning is small. Fraction B appears to crystallize primarily in an octahedral form. Fraction C occurs as multiple twinned prisms, and fraction D in very dense rosettes of small, lobe-like prisms. Crystals of fractions E and F have not yet been obtained.

DISCUSSION

It should be emphasized at the outset that the second form upon which the H isomerism of tetraphenylporphine was postulated has not been found under the conditions used in this investigation. That is, we have not isolated an isomeric compound of chemical composition conforming to tetraphenylporphine, $C_{44}H_{30}N_{4}$, of acid number 8, and absorption spectrum similar to the compound with acid number 13.5 but shifted to the blue. (No analytical data were presented in the original publication to indicate a true isomerism, reference being made to the absorption spectra and the analogous porphines.) We have found, instead, at least two (and possibly six) isomers with empirical formula corresponding to that of tetraphenylporphine. The higher number of isomers is a distinct possibility, since fractions C to F (together) formed approximately 10% of the yield of porphyrin-like material, and since the analysis for the unseparated components corresponded to that of $C_{44}H_{30}N_4$. That this analysis might be the result of a fortuitous mixture of different substances is recognized as a possibility, though not a likely one. In this case, a type of isomerism must be proposed which is different from that of mere H isomerism, where only two possibilities have been proposed.

Numerous investigations (for example, refs. 4, 5, 7, 10) of the fine structure of the porphyrin nucleus have not yet brought about complete agreement. Indeed, only two facts have been universally accepted, the empirical formula and the complete conjugation of the ring. The difficulties revolve about the equivalence of the pyrrole nuclei and, as a corollary, the nitrogens within them. The fact that fully symmetrical porphyrins such as 1,2,3,4,5,6,7,8-octamethylporphine (7) exist only as a single compound, and on the other hand, the expected number of isomers (on a resonance basis) are obtained from the unsymmetrical, e.g. copro-porphyrins I, II, III, and IV (7), shows that (a) the pyrroles are equivalent, (b) the double bonds are not static. The latter is also inferred from the general "aromatic" character of porphyrins. The appearance of two spectral types for dicarbonyl-substituted porphyrins (16) (depending on whether they are on opposite or adjacent nuclei) is to be expected, in a manner corresponding to spectral differences of homologous o_{-} , m_{-} , and p_{-} benzene derivatives, and does not demonstrate, as Fischer, and Stern and Wenderlein (16) claim, the inequality of the pyrrolic nuclei.

In an effort to represent the complete equivalence of the pyrroles, Clar and Haurowitz (4) proposed the biradical structure.



The diamagnetic nature of the porphyrins (8) has shown this to be incorrect as such. To account for the diamagnetism they proposed a resonating molecule with one N having an unshared pair of electrons and the other N being only divalent. It is indeed sufficient to represent the equality of the pyrrolic nuclei by describing the actual molecules as being in a state of resonance between the four main forms and various ionic and separated electron forms (3).



If the hydrogen atoms are centrally located, all four structures (IV, V, VI, and VII) will be equivalent. If, however, they are not centrally located then IV and V would constitute the resonance pair of one isomer, while VI and VII would constitute the other. Therefore conjugation and resonance do not, *per se*, preclude the possibility of H isomerism. It does fix the isomerism to either of two types, (a) the adjacent-opposite type (VI, VII and IV, V), or (b) a planar



ring) type. This latter type would necessitate a directional rigidity of the bonds from nitrogen far beyond any possible extrapolation of what has been found. [Witness the inability to obtain geometrical or optical isomers of any primary, secondary, or tertiary nitrogen based upon the tetrahedral or pyramidal allocation of nitrogen valence (15)]. Were the isomerism to be of the adjacent or opposite type, then in an unsymmetrical porphyrin we would expect not two, but six isomers (only two in a symmetrical).



Isomers of this type have never been isolated. Nor are they to be expected since the energy barrier between two such similar forms would hardly seem sufficient to permit separation. Known cases of H isomerism usually involve considerable migration of that atom, whereas in this case it would not even move the entire distance of its Van der Waal's radius.

Two additional facts may be noted from Robertson's (11) x-ray data on the similar phthalocyanins. First, the evidence is that the hydrogen atoms are bonded to a pair of nitrogen atoms rather than to any single nitrogen atom and, secondly, that all C—N distances in the conjugated ring are the same. This indicates that the pyrrolic nitrogen atoms are equivalent.

We are confronted by the existence of at least two, and possibly six isomers for the porphyrin-like substances of empirical formula $C_{44}H_{30}N_4$. From the chemical and physical properties we would presume that the molecules are highly conjugated, aromatic, ringed, generally dibasic, or tribasic. They need not all be porphyrins. Indeed, the following seven methine substituted compounds corresponding to $R_4C_{20}H_{10}N_4$ may be postulated⁷:



The formulas shown above do not exhaust the structure corresponding to $R_4C_{20}H_{20}N_4$. E.g., there are XXI and XXII.



⁷ Were the porphyrin-like components B, C, D, E, F, to correspond to XV, XVI, XVII, XVIII, and XIX or XX, the term carboporphyrins would be proposed. XVI would be carbo-III-porphine, XVII would be carbo-III, IV-porphine, etc.

These compounds, however, are in themselves much less stable than those predicted above, and involve rearrangements exceeding the present known types. More probable than these would be isomers involving phenyl substitution on the β -pyrrole positions, *e.g.*, XXIII and XXIV.



These rearrangements are also considered as too drastic to have occurred to any appreciable extent.

Another possibility for component B is XXV.



Although this is not isomeric with the porphin, differing by 2 hydrogen atoms (H, 4.61 as compared with H, 4.92), analysis of the mixture would not distinguish it, since it would be present at a maximum of about one-third the total yield. The analysis of the separated B however, gives H, 4.89, 4.95, and hence eliminates XXV as a possibility.

Since the α positions in pyrrole are more reactive than the β , formula XIV is assumed to be the main product. A single condensation in the β -position produces formula XV, and this would then be the most likely formula for component B. The statistical probability of two β -condensations would be much

smaller than that for one, a fact which conforms with the low yields of components C, D, E, and F.

The assignment of formula XIV to component A as compared with component B is based on the following facts: (a) the similarity of its absorption spectrum to those of known porphyrins having no chromophoric β substituents. It is to be noted that porphine itself not only has not a 4,3,2,1 spectrum, but Rothemund's and Fischer's compounds differ in the presence of a double band in the former's products at *ca*. 6800 Å. There remains the possibility that these are still mixtures of the types indicated above; (b) the much smaller separation of the first two dissociation constants of the symmetrical form represented by XIV (A) as compared with the wider separation to be expected from XV and found in B; (c) the greater base strength of B is more reasonably to be expected from the unsymmetrical form (XV); (d) the greater stability of the symmetrical form in concentrated sulfuric acid; (e) the smaller solubility of the hydrochloride in water and the free base in ethanol as compared with component B, (f) the smaller number of absorption bands of the Cu-complex might also be correlated with a more symmetrical compound.

Were one to prepare sufficient amounts of both components, one could distinguish between them by the following additional methods:

1. Dipole moments. Component A would be zero, B would be $\neq 0$. In the latter, however, the dipole moment might not be very large.

2. X-ray data. Component A should show the space-group of a centro-symmetrical molecule; component B might not. It is felt that the substitution of -C = for -N = in the nucleus would result in greater x-ray changes than the H

corresponding replacement in the outer portion of the conjugated ring [which is known to have very little effect (17)].

3. Rate of formation of metal complexes. Component A would be expected to be more rapid than B (also more stable.)

4. Isomerism of mono- β -substituted compounds. Component A would produce one; component B would produce seven.

5. Oxidation. Oxidation of component A would not yield β -substituted pyrroles; component B would.

SUMMARY

1. The reaction of pyrrole with benzaldehyde yields six porphyrin-like compounds which may be separated chromatographically. At present they may be distinguished, when separated, by absorption spectra and crystal forms.

2. At least two of these, and possibly all six, are isomeric. The two known isomers are not interconvertible by means of their copper complexes or their hydrochlorides. Their acid numbers (for the respective fractions A and B) are 13.5 and 19.5. Various distinguishing properties, including polybasicity are discussed. A method for spectroscopic determination of polybasic ionization constants in a system with more than two molecular species is presented. The absorption spectra of the copper salts of fractions A and B are given.

3. The nature of the porphyrin nucleus is discussed. The possible structure of these isomers is presented and a new class of compound, carboporphines, is proposed.

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