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ANNOTATED BIBLIOGRAPHY OF ALPHA, BETA, GAMMA, DELTA-TETRAPHENYLPORPHINE

by

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This annotated bibliography on alpha, beta, gamma, delta-tetraphenylporphine has been prepared as a reference for analytical research. The authors hope that this bibliography will be of service to those engaged in research and development work and that further work on the analytical applications of this interesting reagent may be encouraged by the availability of this reference.

The references in this bibliography deal with the methods of preparation and purification of alpha, beta, gamma, delta-tetraphenylporphine, the properties of some of its metal complex salts, and its analytical applications. The references are listed chronologically.

1936


The molecular absorption coefficients of porphin and four ms-substituted porphines have been measured throughout the visible region, and the curves showing absorption coefficient as a function of wavelength are shown. All of the substances have a very strong absorption band at the violet end of the visible region. The rest of the spectrum, while similar in pattern for all the substances, shows some characteristic differences.
Chlorophyll a or b is added to tetralin and heated to 125°C. A red chemiluminescence is just perceptible; increasing the temperature increases the intensity, exhibiting a red glow at 160 to 1900°C, then disappears when soln. is boiled for a few minutes. Addition of more chlorophyll to the hot soln. causes chemiluminescence to reappear. The Mg and Zn complex salts of porphine and \( \alpha, \beta, \gamma, \delta \)-tetraphenylporphine react in the same manner and give the same color. The free porphines and \( \alpha, \beta, \gamma, \delta \)-tetraphenylporphine or their hemins, Cu, Ni, Co, or Ag complex salts give a negative reaction. When Mg is added to a solution of \( \alpha, \beta, \gamma, \delta \)-tetraphenylporphine in tetralin and allowed to stand for some time, the chemiluminescence can be observed upon heating. No change of color or intensity occurs on bubbling \( \text{O}_2 \) or \( \text{CO}_2 \) through the hot soln. Xylene, \( \text{F-cymene} \) or bromo-cyclohexane may be used as solvents for porphyrin, Mg, or Zn complex salts. After the reaction the soln. differs spectroscopically from the unheated soln.

In the prepn. of porphin from pyrrole and formaldehyd the reaction mixture contained in addition to porphin, a porphyrin with a hydrochloric acid number lower than that of porphin. In comparison with porphin the two main absorption bands of this porphyrin were shifted about 100 Å toward the red region of the spectrum. The new porphyrin is formed only in small quantities; its \( \text{HCl} \) No. was 0.5 while porphine, the main product had an \( \text{HCl} \) No. of 3.3. The elementary analyses checked with each other within exptl. errors. Each formed complex salts with Mg, Fe and Cu. The new porphyrin was given the name isoporphine. One absolute configuration cannot be assigned to either compound.
\( \alpha, \beta, \gamma, \delta \)-tetraporphiline was synthesized and shown to consist of two isomers, \( \alpha \) and \( \beta \).

**Porphine**

**Isoporphine**

The absorption spectra of $\alpha$, $\beta$, $\gamma$, $\delta$-tetraphenylporphine and the Cd, Ag, Zn, Pb, Ni, Co, FeCl$_3$, MnCl and SnCl$_2$ complex salts have been studied over the region from 900 $\mu$ to 370 $\mu$ in benzene solution, using a recording spectroradiometer. There were no absorption bands observed in any of these substances between 900 $\mu$ and 700 $\mu$. All, however, showed characteristic absorption in the visible region. Absorption curves, showing molecular absorption coefficients as a function of wavelength have been determined for all these substances from 700 $\mu$ to 370 $\mu$.


The fluorescence spectrum of $\alpha$, $\beta$, $\gamma$, $\delta$-tetraphenylporphine in anhydrous benzene and under an atmosphere of nitrogen has been photographed. The spectra of the Ni, FeCl$_3$, and Ag complex salts have also been photographed under similar conditions. A fluorescence band was observed with its maximum at 655 $\mu$ for each of these substances. This same band is also observed for tetraphenylporphine under an atmosphere of carbon dioxide. Two additional bands have also been observed in the near infra-red for tetraphenylporphine.

Heating 10 ml of pyrrole, 20 ml of benzaldehyde and 20 ml of pyridine in a nitrogen atm in special Carius tubes at 220°C for 48 hrs gives 1.7 - 2 gm of \( \alpha, \beta, \gamma, \delta \) -tetraphenylporphine, bluish-red needles, M. P. 450°C; HCl No. 13.5; the solubility is 35 mg/100 ml in glacial AcOH and approx. 250 mg in 100 ml 90% HCO\(_3\)H. Its acid solutions are bright green and exhibit a characteristic acid porphyrin spectrum; solutions in other solvents are magenta-red with red fluorescence. In HCl, it gives an amorphous HCl salt of indefinite compn.; it decomposes slowly on standing and rapidly in the presence of moisture. The absorption spectra of \( \alpha, \beta, \gamma, \delta \) -tetraphenylporphine in ether, CHCl\(_3\), C\(_6\)H\(_5\)N, CHCl\(_3\)-HCl, AcOH and 21% HCl are given. In its prep. an isomer is formed. (HCl No. 8.5)


The molar absorption coefficients of ms-tetraphenylporphine and the Cu, Ag\(_2\), Zn, Cd, Hg, SnCl\(_2\), Pb, MnCl, FeCl, Co and Ni complex salts were measured (360 - 400 mu). Curves are shown.

1942


The more abundant isomer of ms-tetraphenylporphine was found to have a polarization of 310 and an electronic polarization of 297. Measurements of polarization at different temperatures gave no indication of a decrease in polarization with increasing temperature. Both methods indicate that the compound has zero moment, although the data do not permit distinguishing between a moment of a few tenths and a zero moment.
1943


When 5 cc of pyrrole and 10 cc of pyridine are heated at 100°, 165°, 190°, 220° and 245° for from 5 days at the lowest temperature to 18 hours for the highest, up to 10% (48 hours at 190° to 220°) purple crystals of a porphyrin mixture of the compound \(\text{C}_{44}\text{H}_{30}\text{N}_{4}\) (\(\alpha, \beta, \gamma, \delta\)-tetraphenylporphine) are obtained. The mixture is fractionated chromatographically using talc as absorbent and \(\text{Cl}_{2}:\text{CHCl}\) as solvent.

1944

10. Calvin, M., Ball, R. H. and Aronoff, S., "\(\alpha, \beta, \gamma, \delta\)-Tetraphenylchlorine," J. Am. Chem. Soc., 65, 2259 (1943), cf. C. A., 37, 5068 (9) \(\subseteq\) C. A., 38, 95 (8) (1944)

In the prepn. of tetraphenylporphine from pyrrole and benzaldehyde (cf. Rothemund, C. A., 34, 439 (8)), the spectra of the resulting compounds indicated that the first two most abundant products might be related as porphyrin to chlorine. It is shown that these products are related by oxidation and reduction and thus the next most abundant product is considered to be tetraphenylchlorine.

1947


The main products from 5 cc pyrrole and 10 cc each of benzaldehyde and pyridine are \(\alpha, \beta, \gamma, \delta\) - tetraphenylporphine, \(\text{C}_{44}\text{H}_{30}\text{N}_{4}\), and \(\alpha, \beta, \gamma, \delta\) - tetraphenylchlorin, \(\text{C}_{44}\text{H}_{32}\text{N}_{4}\). The yield of the latter is better at higher temps. (4% at 170°, 12% at 200°, and 20 to 5% at 220°). The
addn. of 5 gm of Zn(OAc)$_2$ to the reaction mix. increases yield from 4-5 to 10-11% (based on pyrrole); the product in this case is the Zn complex of $\alpha$, $\beta$, $\gamma$, $\delta$-tetraphenylporphine which upon treatment with 6N HCl yields practically pure $\alpha$, $\beta$, $\gamma$, $\delta$-tetraphenylporphine. The tetraphenylporphine and the tetraphenylchlorin can be sepd. by chromatography on talc from ClCH:CCl$_2$ (max. of 9 mg/sq cm of cross sect. area of column). The Cu salt of the tetraphenylchlorin is oxidized to that of the tetraphenylporphine by a mole of O. The Zn salt of the tetraphenylporphine can be reduced by Na in ethanol to that of the tetraphenylchlorin. Hydrogenation of the tetraphenylporphine gives the tetraphenylchlorin. These reactions are not complete and their course is followed by absorption curves. The structures of the tetraphenylporphine and the chlorin are confirmed by direct analysis.

1948


When the Zn salt of tetraphenylchlorin was allowed to stand for a few hours the green color of the solution, which gave a red fluorescence, changed to a yellow colored solution with no fluorescence. An absorption spectrum of such a solution showed the Zn chlorin band still existing at 6200 A$, the formation of a Zn chlorin band at 5500 A$, also the formation of some new substance with a high absorption in the region 4650 A$. The degradation was found to be caused by a light induced oxidation by molecular oxygen. Other oxidizing agents gave the same result. Ortho and para quinones in a deoxygenated benzene solution was found to give a quantitative yeild of only one product, Zn tetraphenylporphine.

Salts of α, β, γ, δ-tetraphenylporphine are prepd. in AcOH or HCO₂H with the acetate of the metal, in hot C₆H₅N, or in 40% MeOH-KOH. In the formulas, R = C₅H₁₂N₄. The salts analyzed are RCu, RHAg, RAg₂, RAu₂Cl₄, RMg, RH₂MgO, RZn (C₅H₁₂N₄Zn given), RCd, C₅H₁₂N (?), original gives C₅H₁₂Cd·C₅H₁₂N), RCo, RHg, RTl, RSnCl₂, RPb C₅H₁₂N, RMnCl, RFeCl, RCo, and RNi; qualitative and solubility data are given. Absorption max. are given for the above salts and also Li, Na, K and Rb. The salts have high surface luster, show selective adsorption in the visible region of the spectrum and melt from 400 to 500°; all except MnCl and Au₂Cl₄ salts sublime from 400 to 450° with partial decompn. of complex. The K and Tl complexes decompn. in C₆H₆ or ether; the Mg, Hg and Pb complexes split when shaken with 50% AcOH; the Zn and Ag complexes are stable in 50% AcOH but decompn. slowly in HCl; the other salts are stable to concd. HCl on the steam bath. The complexes of Li, Na, K, Rb, and Ce decompn. rapidly when exposed to strong light; the Mg and Tl compds. showed spectrum shifts under these conditions. The Zn, Mg and Cd salts showed a bright red chemiluminescence when heated above 125° in tetralin, xylene, p-cymene, or bromocyclohexane. When freshly distilled tetralin is used, only a faint glow of short duration is observed; on adding a few drops of tetralin which has been standing for some time, the bright red glow reappeared.

1949

The Zn and Mg complexes of tetraphenylchlorin can be photooxidized to the corresponding porphines by ortho and para-quinones. Plotting of the quantum number against the standard oxidation potential yields one straight line for the o-quinones and another straight line for the p-quinones. The rate of the Zn chlorin reaction is faster than the Mg by a factor of almost 8.


Zinc and magnesium tetraphenylchlorins can be photooxidized by oxygen to the corresponding porphine. A secondary reaction occurs between H₂O₂ and the porphin, yielding a product similar to that obtained by "bleaching" chlorophyll in the presence of O₂.

1950


The metalloporphines derived from the smaller bivalent metals are in general quite resistant to hydrolysis. Replacement reactions, however, are possible as shown by conversion of the Zn salt into the Cu salt by prolonged heating with cupric acetate. The smaller bivalent metalloporphines also have similar spectra. The spectra of the large bivalent metalloporphines differ from the smaller bivalent metals and undergo replacement reactions as follows: Pb or Hg in a metalloporphine is replaced quantitatively by a smaller bivalent metal such as Zn or Cu and the larger Pb ion is replaced by a Hg ion. Even with a large excess of inorganic metal ion the reaction does not go in the reverse direction. The porphine salts of the alkali metals are readily hydrolyzed by H₂O, and exhibit a spectra in the case of α, β, γ, δ-tetraphenylporphine similar to Pb and Hg, and undergo replacement reactions as follows: The alkali metal ions in an alkali metalloporphine are rapidly and completely replaced by a smaller bivalent ion, a large bivalent ion,
or a smaller alkali metal ion. None of these reactions proceed in the reverse direction even in an excess of inorganic metal ion. Complete equilibrium of the activity in a pyridine solution of NaI and di-Na tetraphenylporphine is observed at room temp. in less than 6 minutes.

1951


The absorption spectra of 17 different metallo derivatives of α, β, γ, δ-tetraphenylporphine are correlated with the nature of the bonding between the central metal constituent and the N atoms on the porphine ring. Methods of preparation and details of certain chemical properties of the metallophenylporphines are described; phosphorescence, fluorescence, and absorption spectra of the tetraphenylporphine compounds are given.

1952


The absorption spectra of α, β, γ, δ-tetraphenylchlorine and some of its metallo complex derivatives are given. A method is given for the separation of α, β, γ, δ-tetraphenylchlorine (I) and α, β, γ, δ-tetraphenylporphine (II); to a mixture (400 mg of (I) and (II) free bases prepared by heating benzaldehyde, pyrrole, and pyridine in a sealed tube 36-38 hrs. at 200 to 220°) in the min. atm. of C2HCl3, was added 1 gm zinc acetate, and the mixt. heated gently (the course of the reaction was followed visually with a spectroscope) until all of the (II)
was converted to the Zn derivative, then absorbed on a talc column and developed with \( \text{C}_2\text{H}_5\text{CHCl}_3 \); the Zn derivative of (II) passed through quickly, leaving on the column the free (I) which was eluted with acetone, 20 cc \( \text{C}_2\text{H}_5\text{CHCl}_3 \) added to the eluant, the resulting soln. was washed with \( \text{H}_2\text{O} \), treated with 25 cc 8N HCl, neutralized with 6N \( \text{NH}_4\text{OH} \), washed again several times with \( \text{H}_2\text{O} \), dried with \( \text{Na}_2\text{SO}_4 \), and chromatographed again to give a high purity of (I). All metal derivatives of (I) are unstable to light induced oxidations by molecular oxygen, some are even unstable in the solid state.


The complex formation of the Mg, Zn, Cd, Hg and Cu II derivatives of \( \alpha, \beta, \gamma, \delta \) -tetraphenylporphine (I) and \( \alpha, \beta, \gamma, \delta \) -tetraphenylchlorine (II) with pyridine was investigated by determining the optical density of any wave length at which the complexed and uncomplexed derivatives differed appreciably. The Mg derivatives of (I) and (II) formed dipyridinates, whereas all other metal derivatives formed monopyridinates. The equilibrium constants, \( \Delta H \text{cal/mole} \), and the standard entropy changes, which were all negative, were determined in all cases. The absorption spectra of each complex of (I) and (II) were run in \( \text{C}_6\text{H}_6 \) and pyridine or a mixture of the two. The Co(III) derivative of (I) chloride monopyridinate is not appreciably dissociated at a concentration of \( 4 \times 10^{-5} \) M, which corresponds to an association constant of greater than \( 10^{7} \). The Cu(II) derivative of (I) forms a monopyridinate with an association constant at 30°C of about 0.05, similar to that of the Ni(II) derivative, whereas the Ag(II) derivative is a much weaker Lewis acid toward pyridine.

1953

This paper is about the reduction of Zn tetraphenylporphine by a series of ene-diol and related compounds. The reduction products were identified as Zn tetraphenylchlorine (dihydroporphine) and Zn tetrahydrotetraphenylporphine. The spectrum of the latter was established. The reduction was carried out in the presence of light. Some of the reducing agents were benzoin, p-dimethylamino-benzoin, ascorbic acid, dihydroxyacetone, reductone and dihydroxymaleic acid. The kinetics of the fastest reaction, benzoin, was studied. The reaction rate was directly proportional to the light absorbed by the benzoin but dependent on the light absorbed by Zn tetraphenylporphine. The photo-oxidation of Zn tetrahydrotetraphenylporphine to Zn tetraphenylporphine was also studied. The nature of the metal in the center of the porphyrin ring was correlated with the fluorescence, magnetic susceptibility, and the stability of the metal porphyrin complex.


Metallic complexes of phthalocyanine dyes function as catalase models for the decomposition of peroxides. In hot hydrocarbon solvents, a bright chemiluminescence accompanies these decompositions. The decomposition of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide(I) by Zn tetraphenylporphine(II) in tert-butylbenzene at 149° was studied. It was found that (1) initial increase in rate of (I) (over uncatalyzed (I) is proportional to initial concentration of (II); (2) d(II)/dt = k₀(II) (I), where k₀ = 0.5 ± 0.1 l. mole⁻¹ min⁻¹; (3) the turn-over No. was 20-30 mol. of I per mole of II; (4) luminescence intensity = k (I) (II); (5) reaction products were found to be 3,4-dihydro-1-(2H)-naphthalenone and water; (6) with II as catalyst, cumene hydroperoxide and ter-butyl peroxide gave only feeble emission; di-tert-butyl peroxide gave no emission.
1954


The tarry product from the reaction of pyrrole and benzaldehyde and zinc acetate in pyridine was extracted with acetone and crystalline Zn tetraphenylporphine obtained. It was found that about 5 gm of the complex was lost for each liter of acetone. The new method depended upon decomposing the complex with acid and chromatographing the free base tar solution on \( \text{Al}_2\text{O}_3 \). The free base-eluante was chromatographed on Magnesol to yield pure tetraphenylporphine.


Besides the spectra of microorganisms, the spectrum of Zn tetraphenylporphine in the powdered form was also obtained and the curves compared with those obtained in solution. The technique consisted of providing the sample and blank cell compartments, on the sides of light transmission, with identical opalescent plates which uniformly diffuse all of the light as it leaves the cuvets.

1955


In the conversion of tetraphenylchlorine(I) to tetraphenyl-tetrahydroporphine(II) by catalytic hydrogenation, two compounds (III) and (IV) were isolated from the reaction. (I) (100 cc, 2 x 10\(^{-4}\) M in ether) stirred 30 min. under H at 1 atm. with 0.1 cc freshly prepared Raney Ni, the Ni filtered off, (I) removed from the
filtrate by 8-10 extractions with 100-cc portions of 5N HCl in a minimum of light, the ether solution washed with water, 6N NH₄OH and water, evaporated to dryness in vacuum, and the residue in a minimum of Cl₂CHCl chromatographed on talc yielded 2-4% (III). (III) with EtMgl yields the Mg derivative. (IV) is formed in the above described reaction but the yield is improved if the reduction is carried out with 0.2 gm Raney Ni in 20 cc dioxane. (IV) is obtained in 2% yield contaminated with 5-10% (I). (III) is identified tentatively as tetrahydroporphine. (IV) may be a tetrahydroporphine with adjacent pyrroles reduced, but some of its properties are similar to those of a chlorin. Absorption spectra are presented and discussed.


The kinetics of the photoreduction of Zn tetraphenylporphine by benzoin was studied. The products were successively the dehydro(chlorin) derivative, a tetrahydro derivative, and possibly a hexahydro compound. The primary requirement is the photoactivation of benzpin; a secondary reaction, involving photoactivated porphyrin, was also demonstrated. The quantum yield based on light absorbed by benzoin varied between 0.01 and 0.06.

1956


This paper gives the method for synthesizing para-methyl, methoxy, chloro and nitro derivatives of tetraphenylporphine directly from pyrrole and the corresponding aldehyde. Chlorins and other by-products were separated chromatographically and characterized by spectrophotometric analysis. The yields of main product decrease as the acceptor activity of the aldehyde carbonyl increases.

The absorption spectra of tetraphenylporphine, tetra-(p-methoxyphenyl)-porphine, tetra-p-tolyl porphine, tetra-(p-chlorphenyl)-porphine and tetra-(p-nitrophenyl)-porphine in the ultraviolet, visible and infrared regions are reported. The visible and ultraviolet spectra indicate that the para-substituent exert only a small effect on the electronic transitions of the porphine ring system. Assignments of infra-red frequencies are made where possible.

1957


The zinc complex salt of \( \alpha, \beta, \gamma, \delta \)-tetraphenylporphine has a strong absorption band at 551 \( \mu \)m. When zinc acetate is added to a solution of \( \alpha, \beta, \gamma, \delta \)-tetraphenylporphine in glacial acetic acid, the following equilibrium is established in 60 to 70 minutes at room temperature:

\[
\text{Zn}^{++} + \text{TPPH}_2 = \text{ZnTPP} + 2\text{H}^+.
\]

The addition of an acetate salt functions as a base and shifts the equilibrium to the right. However, when the maximum amount of zinc present is complexed, addition of more acetate salt reverses the equilibrium. Curves are given showing absorbance versus ionic strength. A method is also given for indirect determinations of several other metals in certain compounds.