[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF WASHINGTON UNIVERSITY AND THE UNIVERSITY OF CALIFORNIA]

The Spectra of α,β,γ,δ-Tetraphenylchlorin and its Metallo-derivatives

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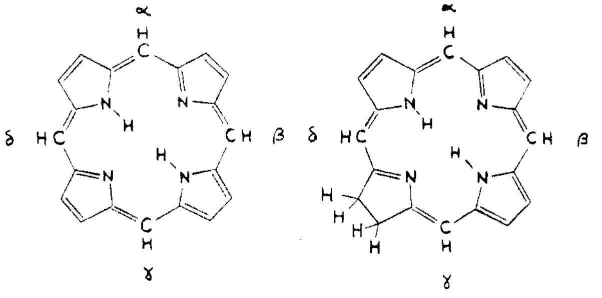
An improved method is described for the synthesis of α,β,γ,δ-tetraphenylchlorin, a model compound related to chlorophyll. Nine metallo-derivatives of this compound have been prepared and their absorption spectra measured; fluorescence and phosphorescence spectra are reported for the zinc and magnesium derivatives. On the basis of the calculated oscillator strengths for the first two electronic transitions, the absorption spectra are discussed briefly.

In a previous paper[1] the oscillator strengths and other characteristics of the absorption spectra of various metallo-derivatives of α,β,γ,δ-tetraphenylporphine were presented. Partial reduction of this porphine by the addition of two hydrogen atoms across one of the "semi-isolated" double bonds gives rise to the corresponding chlorin[2] (*cf.* Fig. 1), which is related to the chlorophylls in the sense that both are derivatives of the fundamental chlorin ring system. The metallo-derivatives of tetraphenylchlorin, while similar in many respects to those of the corresponding porphine, possess several new and interesting properties. The present paper is concerned with the preparation and spectra of these metallochlorins.



a. Porphine ring. b. Chlorin ring.

Fig. 1.—Porphyrin structures.

Experimental

Preparation of Tetraphenylchlorin (Free Base).—Pyrrole and benzaldehyde, when heated together in a pyridine solution, produce a mixture of tetraphenylporphine and tetraphenylchlorin.[3] The yield of the chlorin, which constitutes about 20% of the porphine–chlorin mixture under the best conditions, is only about 1% over-all (based on the pyrrole). Despite the low yield and the difficulty of separating the chlorin from the relatively large amount of porphine, we have been more successful in obtaining appreciable quantities of tetraphenylchlorin by isolating it directly from the above synthesis mixture than by methods which employ a direct reduction of the more plentifully available tetraphenylporphine.[4] Some improvements in the tedious chromatographic separation of the chlorin previously reported[3] have been effected, and are incorporated into the following revised procedure:

Four hundred mg. of a mixture of tetraphenylporphine and tetraphenylchlorin free bases (prepared by heating benzaldehyde, pyrrole and pyridine in a closed tube at 200–220° for 36–48 hours as previously described[3]) are dissolved in a minimum of redistilled trichloroethylene, about 1 g. of zinc acetate is added, and the solution heated gently. The free base porphine is rapidly converted to zinc tetraphenylporphine, while tetraphenylchlorin is only slowly converted. By following the course of the reaction in a visual spectroscope, the reaction may be stopped (by rapid cooling) when all of the porphine but only a small portion of the chlorin has been converted to the zinc derivative. A short chromatographic column 3.5 inches in diameter and 4 inches in depth (*e.g.*, a large sintered glass funnel) is filled with talc and tightly packed with the aid of tamping and vacuum. The trichloroethylene solution is chromatographed on this column with fresh trichloroethylene as the developing solvent. The zinc tetraphenylporphine passes through quickly, leaving the free base chlorin on the column. The small amount of zinc chlorin present follows the zinc porphine through the column, and provides a convenient indicator for ceasing the operation. (The zinc chlorin is easily recognizable by its green color and very strong red fluorescence.) The chlorin is eluted from the column with acetone, and 20 cc. of trichloroethylene added to the eluent. The resulting solution is washed with water to remove the acetone, treated with 25 cc. of 8 *N* hydrochloric acid, neutralized with 6 *N* ammonium hydroxide, washed several times again with water, and dried over anhydrous sodium sulfate. This treatment converts any zinc chlorin to the free base, and results in a trichloroethylene solution of tetraphenylchlorin containing only 10–20% porphine. A single chromatographing of this material, in the manner described previously[3] will lead to tetraphenylchlorin of high purity.

Preparation of Metallo-tetraphenylchlorins—The zinc, cadmium, silver(II), tin(II) and cobalt(II) derivatives of tetraphenylchlorin may be prepared by the previous method[1] for the corresponding metalloporphines with the exception that the reaction solvents are not the same. The difference is due to the fact that oxidation of the chlorin to the porphine often occurs when glacial acetic acid is the solvent, so that this solvent is preferably avoided when making chlorin derivatives. The extent to which oxidation occurs, and the rate at which it occurs, seems to depend upon the history of the acetic acid; old, opened samples seem to be particularly bad, due perhaps to the presence of peroxides which have slowly accumulated. Except for the tin(II) derivative, which may be prepared only in freshly distilled acetic acid, it is expedient to use other solvents. Dioxane is suitable for Cu(II) and Cd(II); pyridine for Co(II) and Ag(II). The zinc derivative may be prepared in either dioxane or pyridine.

The disodium, magnesium and hydrochloride derivatives are prepared by the methods reported for the porphines.[1]

It should be noted that nearly all the metallochlorins are unstable with respect to light-induced oxidations by molecular oxygen in some solvents, and some are even unstable in the solid state. Since the preparative methods given for the metalloporphines often involve several solvents, it is necessary to carry out the preparations in the minimum of light. In this regard, more of the metallochlorins are photoöxidized in benzene than in any of the other common solvents. The product of these photoöxidations is seldom a single product such as the corresponding porphine, but

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(1) Dorough, Miller and Huennekens, THIS JOURNAL, **73**, 4315 (1951).

(2) The German term "porphin" has been Anglicized to "porphine" in order to give the word an -ine ending characteristic of the English language nomenclature for nitrogen containing organic compounds. It has been suggested to extend the Anglicization to the term "chlorin," but the resulting term "chlorine" is a rather confusing one. We have thus retained the term "chlorin" as have most other workers in the field. For further information on the system of nomenclature employed, see reference 1, footnote 2.

(3) Ball, Dorough and Calvin, THIS JOURNAL, **68**, 2278 (1946).

(4) Prof. H. Linschitz of Syracuse University has informed us that he has had good success with one particular reduction method. Zinc tetraphenylporphine is reduced by sodium in amyl alcohol to give the tetraphenylchlorin, which is then separated from other products by means of chromatography on alumina with benzene as the solvent.

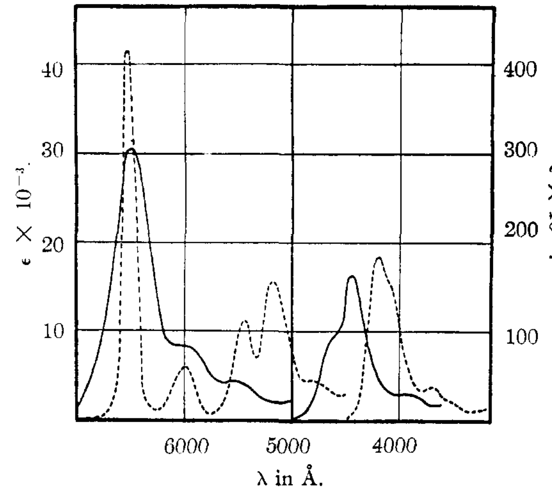


Fig. 2.—Absorption spectra (in benzene): solid line, hydrochloride; dashed line, free base.

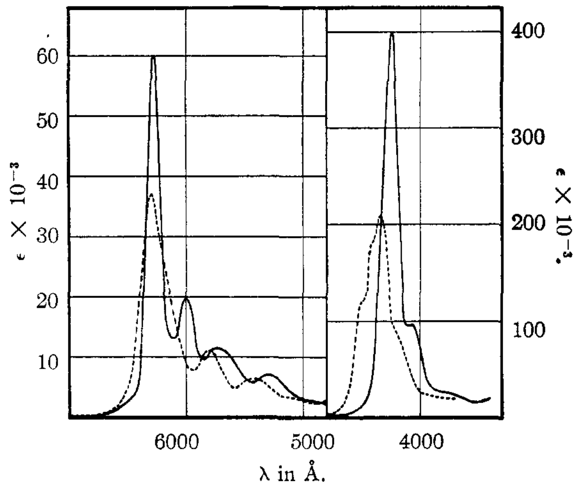


Fig. 3.—Absorption spectra: solid line, magnesium (in benzene); dashed line, disodium (in pyridine–3% methyl alcohol).

usually is a mixture of the porphine and various compounds resulting from cleavage of the ring.[5]

Absorption and Emission Spectra; Oscillator Strengths.—The methods employed for the measurements of these properties were identical to those reported previously.[1]

Discussion

The change from the porphine to the chlorin structure does not alter the general pattern of the absorption spectra of the porphines. In the range 3500 to 7000 Å. there are still two regions of absorption corresponding to two electronic transitions. There does result, however, a change in intensity of the absorption bands; the Soret bands in the blue region of the spectrum (second transition) are considerably decreased, while the first vibrational band of the first transition is very markedly increased. This latter band in the red region of the spectrum is relatively intense, and is responsible for the green colors which characterize many of the chlorins. It is interesting that the decrease in absorption observed in the second electronic transition is almost equally balanced by the increase in absorption in the first electronic transition, so that the sum of the oscillator strengths of the first two transitions is approximately the same for corresponding chlorins and porphines (*cf.* Table I).

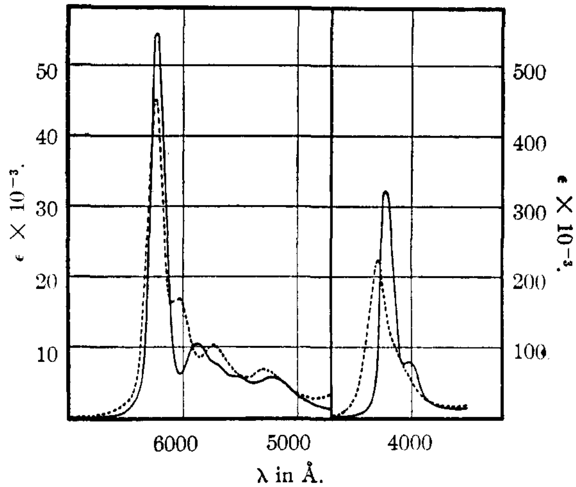


Fig. 4.—Absorption spectra (in benzene): solid line, zinc, dashed line, cadmium.

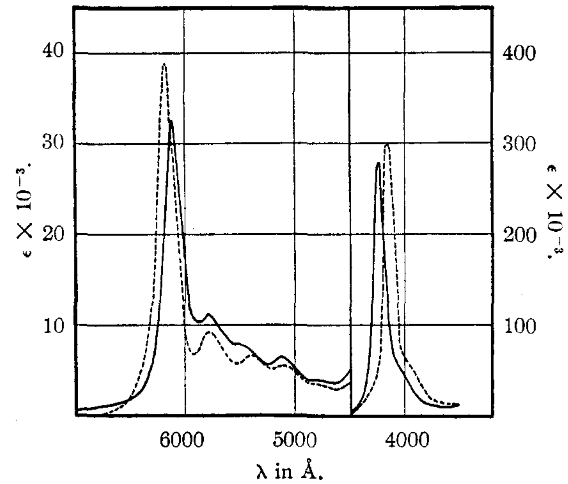


Fig. 5.—Absorption spectra of sub-group I metals (in benzene): solid line, silver(II); dashed line, copper(II).

TABLE I

OSCILLATOR STRENGTHS OF THE METALLOCHLORINS

Central substituent	Tetraphenylchlorin Oscillator strength (f) 1st trans.	Tetraphenylchlorin Oscillator strength (f) 2nd trans.	Tetraphenylchlorin Sum of "f" values for first two transitions	Tetraphenylporphine sum of "f" values for first two transitions
Free base	0.16	1.49	1.65	1.63
Disodium	.17	1.23	1.40	1.42
Magnesium	.19	1.71	1.90	1.74
Zinc	.16	1.30	1.46	1.47
Cadmium	.19	1.27	1.46	1.48
Copper(II)	.18	1.18	1.36	1.37
Silver(II)	.19	1.03	1.22	1.22
Tin(II)	.15	1.05	1.20	1.17
Cobalt(II)	.15	1.03	1.18	1.22

It might be assumed that a set of energy levels derived for the porphine ring by quantum me-

(5) Huennekens and Calvin, THIS JOURNAL, **71**, 4031 (1949).

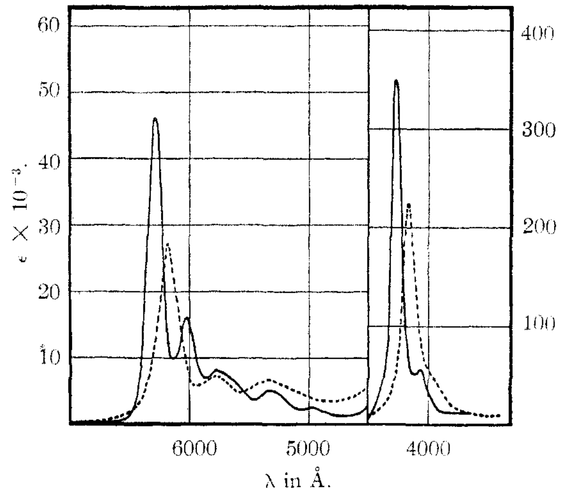
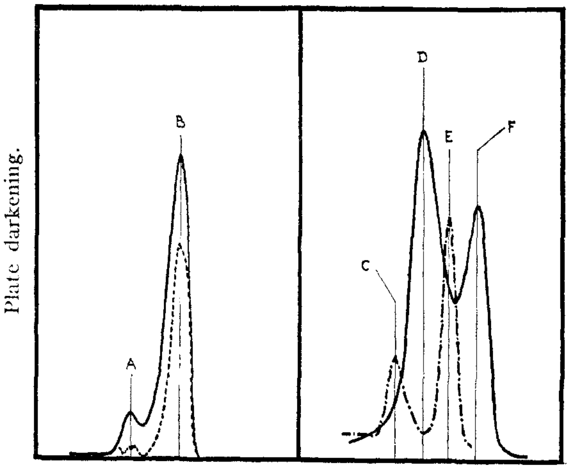


Fig. 6.—Absorption spectra (in benzene): solid line, tin(II); dashed line, cobalt(II).



Phosphorescence (in EPA). Fluorescence (in benzene).

Fig. 7.—Emission spectra: solid line, zinc; dashed line, magnesium; dashed-dotted line, free base. (Peak heights are not relative as shown—see experimental.) Wave lengths in Å.: A, 9000; B, 8000; C, 7300; D, 6900; E, 6600; F, 6250.

chanical methods[6,7] would be applicable to the chlorin ring with the qualification that any degenerate levels would be split, since the addition of the two extra hydrogens would destroy the fourfold symmetry (D_{4h}) assumed for the porphine structure. The fact that the chlorin absorption spectra follow the porphine spectra in pattern and position, and the fact that the sum of the oscillator strengths of the first two transitions are nearly identical would support such a supposition. However, the first two electronic transitions in the porphine are to doubly degenerate levels, so that a splitting of the bands in chlorin spectra would be expected. Such splitting is observed, but in an unusual manner. For example, the absorption corresponding to the second transition in the free base,[8] the hydrochloride and the sodium salt of tetraphenylchlorin consists of split peaks (*cf.* Figs. 2 and 3) which individually are roughly half as high as the large Soret peak of the corresponding porphines (compare with Figs. 3 and 4 of reference 1). However, the lower energy transition for these three cases leads to spectra in which the bands are identical in number and position. Inspection of some of the other metal derivatives (*e.g.*, compare the spectrum of the zinc chlorin in Fig. 4 with Fig. 7 of reference 1) indicates a reverse situation, namely, the bands in the first electronic transition are split but not those in the second. The failure to observe experimentally a splitting in both regions of absorption when the symmetry of the porphine structure is reduced to that of the chlorin would suggest that considerations other than symmetry alone must be taken into account if a porphine set of energy levels is to be applied to the interpretation of chlorin spectra.

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(6) Simpson, *J. Chem. Phys.*, **17**, 1218 (1949).

(7) Longuet-Higgins, Rector and Platt, *ibid.*, **18**, 1174 (1950).

(8) Strictly speaking, the free base porphine is already at a lower symmetry than D_{4h} due to the fact the two center imino hydrogens are not equivalently bonded to all four nitrogens (Corwin and Erdman, THIS JOURNAL, **68**, 1885 (1946); Dorough and Shen, *ibid.*, **72**, 3939 (1950)). Platt has explained the fact that the absorption spectrum corresponding to the first electronic transition of the free base differs markedly from the spectra of metalloporphines of true D_{4h} symmetry by assuming that the transition in the free base is to split levels rather than to a doubly degenerate level (Chapter 4, "Radiation Biology. Volume 3. Biological Effects of Visible Radiation," S. Hendricks, editor, McGraw-Hill Book Co., Inc., to be published, 1952). It is to be noted, however, that there is no evidence of splitting in the second electronic transition of the free base of tetraphenylporphine (as compared to its metallo derivatives), and it is this absorption region which is under discussion above.