

## Spectroscopic Studies of the Simpler Porphyrins I. The Absorption Spectra of Porphin, msMethyl Porphin, msEthyl Porphin, msPropyl Porphin and msPhenyl Porphin

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J. Chem. Phys. **9**, 197 (1941); 10.1063/1.1750879

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the photochemical activity extends still further out. Unfortunately, because of the low absorption of water at these long wave-lengths, the chemical effects are small and it is a matter of considerable difficulty to eliminate or correct for direct photodecomposition.

We have remarked that water is not decomposed under the conditions of irradiation used in the present experiments (Fig. 1). This is what one would expect, in view of the fact that no decomposition is obtained even upon irradiation with x-rays.<sup>3c</sup> Several investigators<sup>7-11</sup> have claimed decomposition occurs under conditions

<sup>7</sup> M. Kernbaum, *Comptes rendus* **149**, 273 (1909).

<sup>8</sup> Thiele, *Zeits. f. angew. Chemie* **22**, 2472 (1909).

<sup>9</sup> A. Coehn, *Ber. chem. Ges.* **43**, 880 (1910).

<sup>10</sup> D. Bertelot and H. Gaudechon, *Comptes rendus* **150**, 1690 (1910).

<sup>11</sup> Tian, *Ann. de physique* [9] **5**, 248 (1916).

of irradiation which would appear to supply considerably less energy in the region below 2000Å, than has been used in the present experiments. In some of these experiments the decomposition of organic and other impurities (compare above) in the irradiated water may have been misinterpreted as a decomposition of the water. One other possibility should also be kept in mind: Water may be decomposed in the presence of certain impurities acting catalytically. This has been found to be the case for x-rays. We recently reported<sup>3b</sup> that traces of the iodide or bromide ion were effective with x-rays in this respect. These particular ions, however, have no action in the case of light.

We wish to thank Mr. D. M. Gallagher for his assistance in this work.

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## Spectroscopic Studies of the Simpler Porphyrins

### I. The Absorption Spectra of Porphin, *ms*-Methyl Porphin, *ms*-Ethyl Porphin, *ms*-Propyl Porphin and *ms*-Phenyl Porphin\*

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(Received March 19, 1936)

The molecular absorption coefficients of porphin and four *ms*-substituted porphins have been measured throughout the visible region and the curves showing absorption coefficient as a function of wave-length 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 of the substances, shows some characteristic differences.

#### INTRODUCTION

IN previous papers,<sup>1, 2</sup> the fluorescence spectra and photodecomposition of the chlorophylls and some of their derivatives were discussed. It was found that the fluorescence spectra of all of the substances studied showed a similar pattern. Because of this, it seemed desirable to make similar studies on simpler chlorophyll derivatives. An ideal series of substances for this

purpose is now available since Dr. Paul Rothemund,<sup>3, 4</sup> at this laboratory, has succeeded in synthesizing porphins from substances of aldehydic function and pyrrole. The formula for porphin, which is formed from pyrrole and formaldehyde, is shown in Fig. 1. This substance is of considerable interest, as it is the simplest form of the ring system of the two biologically important pigments, haemin and chlorophyll. It is apparent from Fig. 1 that two isomeric forms of this substance are possible, one with the

\* This work was done with the experimental cooperation of Mr. Alex Horvath on a special scholarship arrangement.

<sup>1</sup> V. M. Albers and H. V. Knorr, *Cold Spring Harbor Symposia on Quantitative Biology* **3**, 87-97 (1935).

<sup>2</sup> Reference 1, pp. 98-107.

<sup>3</sup> Paul Rothemund, *J. Am. Chem. Soc.* **57**, 2010 (1935).

<sup>4</sup> Paul Rothemund, *J. Am. Chem. Soc.* **58**, 625-627 (1936).

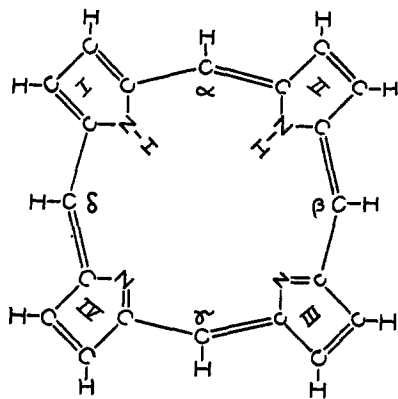


FIG. 1.

hydrogens linked to the nitrogen atoms in adjacent rings, as indicated, and one with the hydrogens linked to the nitrogen atoms in opposite rings with a corresponding rearrangement of the bonds in the ring. In this investiga-

tion the N group has been tentatively as-  
H

sumed to be in rings I and II; further work will show whether this assumption is correct. The system of nomenclature, for these substances, suggested by Rothmund will be followed in this paper, i.e., *ms*-methyl porphin is the porphin with methyl groups substituted for H in the  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  positions. A large number of these synthetic porphins as well as the corresponding phyllins and haemins are now available for study.

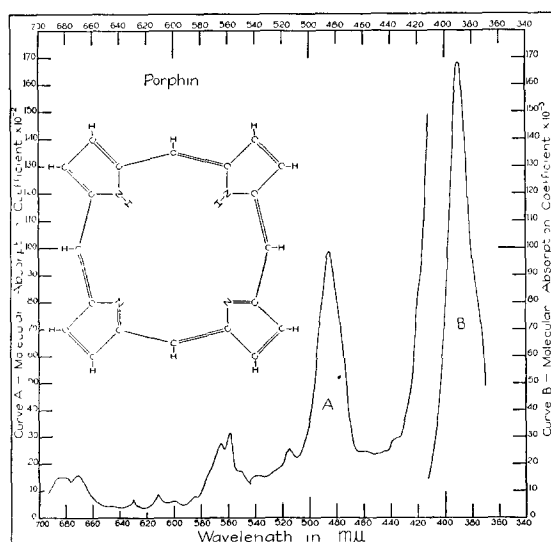


FIG. 2.

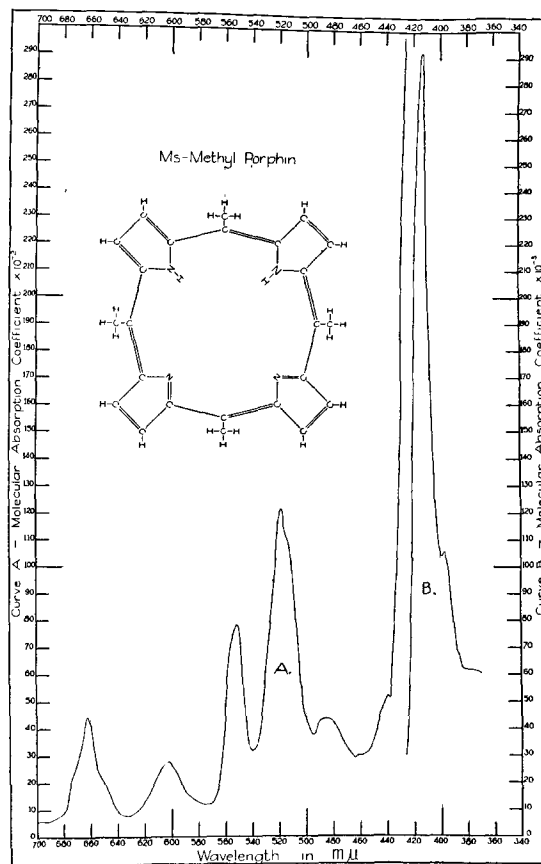


FIG. 3.

This paper will be concerned with measurements of the absorption coefficients throughout the visible region, of ether solutions of porphin, *ms*-methyl porphin, *ms*-ethyl porphin, *ms*-propyl porphin and *ms*-phenyl porphin.

### EXPERIMENTAL

The transmissions of ether solutions of the substances were measured in the region from 370  $m\mu$  to 700  $m\mu$ . The source of continuous radiation was a "photoflood" lamp operated at 120 volts from a motor-generator set. A voltage regulator on the motor-generator set maintained a constant potential difference at the terminals of the lamp. The spectra were photographed with a Hilger E-3 spectrograph using Eastman I-L spectroscopic plates. Each plate was calibrated by making a series of exposures through neutral screens of known transmission, according to the method of Harrison.<sup>5</sup> In all

<sup>5</sup> George Harrison, J. Opt. Soc. Am. **19**, 267-316 (1929).

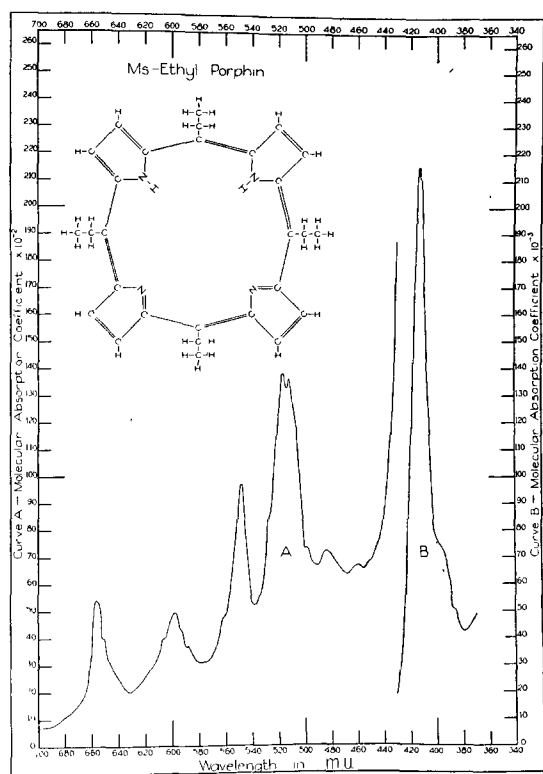


FIG. 4.

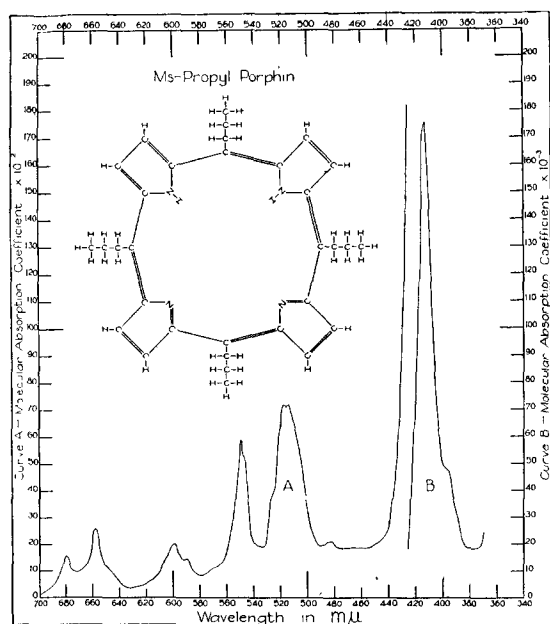


FIG. 5.

cases the exposure times for the calibration and absorption spectra were the same. Because of the great variation in the transmission of the

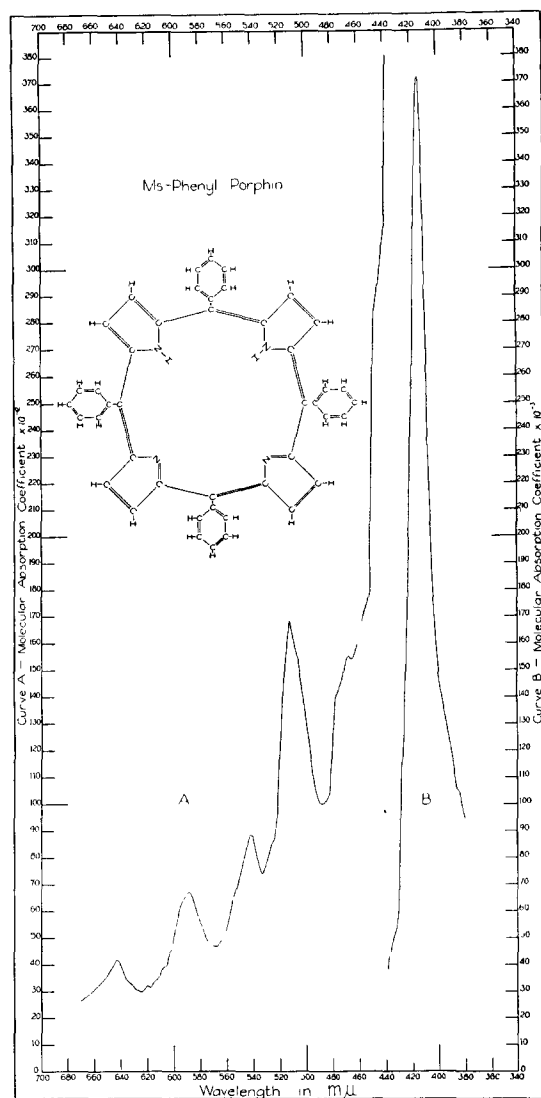


FIG. 6.

solutions, throughout the region investigated, a series of concentrations (in most cases seven) were used, with each successive concentration 50 percent of the one preceding it in the series.

Densitometer curves were obtained for all exposures on a plate, showing galvanometer deflections as a function of wave-length. A characteristic curve was determined for every 50A from the densitometer curves of the spectrograms which were made through the neutral screens. It was found, by trial, that a value of percent transmission for a solution, at a wave-length between those at which the characteristic curves were plotted, could be obtained by inter-

TABLE I.

WAVE-LENGTH (mμ)			WAVE-LENGTH (mμ)			WAVE-LENGTH (mμ)		
<i>a</i>			<i>a</i>			<i>a</i>		
Porphin	390	168 × 10 <sup>3</sup>	<i>ms</i> -methyl porphin	413	292 × 10 <sup>3</sup>	<i>ms</i> -propyl porphin	413	175.5 × 10 <sup>3</sup>
	485	9.83 "		485	4.35 "		483	2.10 "
	515	2.55 "		517	12.2 "		514	7.17 "
	559	3.20 "		551	7.80 "		518	7.17 "
	565	2.73 "		602	2.80 "		549	5.87 "
	585	0.78 "		662	4.45 "		590	1.45 "
	612	0.85 "	<i>ms</i> -ethyl porphin	413	215 × 10 <sup>3</sup>	<i>ms</i> -phenyl porphin	599	2.00 "
	630	0.67 "		460	6.70 "		658	2.57 "
	671	1.57 "		483	7.25 "		680	1.55 "
	683	1.50 "		512	13.6 "		414	372 × 10 <sup>3</sup>
				516	13.8 "		468	15.5 "
				547	9.70 "		512	16.8 "
				597	4.95 "		541	8.85 "
				656	5.40 "		588	6.70 "
							643	4.17 "

polarization from the curves at 50A intervals within the limits of error of reading the curves. The absorption cell filled with pure ether was placed in the light path while the calibration exposures were being made. Therefore, 100 percent transmission represents the transmission of the absorption cell filled with pure ether. The length of the light path in the absorption cell was one cm. The 365-mμ line of Hg was used as a reference line on all exposures for wave-length determinations. The wave-lengths were then read from a previously determined dispersion curve for the spectrograph. With this arrangement, wave-lengths could be consistently read to within ±0.5 mμ at 580 mμ. These limits were established by measurements made on the 577 and 579 mμ lines of Hg.

For the measurements, the pure crystallized substances were dissolved in a small amount of pyridine and adjusted to a suitable concentration by addition of ether. The presence of the small amount of pyridine in the solution does not alter the spectrum from that of the pure ether solution.<sup>6</sup>

The absorption coefficients were calculated using Beer's law in the form of Eq. (1),

$$I_T/I_0 = e^{-acz}, \quad (1)$$

where  $I_T/I_0$  is the ratio of transmission of the absorption cell filled with the solution to the

transmission of the cell filled with pure solvent,  $c$  is the concentration of the solution, measured in moles per liter,  $x$  is the thickness of the absorption cell in cm and  $a$  is the absorption coefficient of the substance.

#### DISCUSSION OF RESULTS

Figs. 2 through 6 show the absorption coefficient curves for the substances, as well as their structural formulae. The outstanding characteristic of the spectra of these substances is a very strong band located in the violet region of the spectrum. This band occurs at 390 mμ in porphin, at 413 mμ in all of the aliphatic substituted meso-porphins, and at 414 mμ in the *ms*-phenyl porphin. It is interesting to note that the absorption coefficients for this band in the aliphatic substituted porphins are larger than the corresponding absorption coefficient for porphin, but that their value decreases as the length of the carbon chain increases. While the general pattern of the spectra in the longer wave-length region is similar for these substances, it is difficult to make direct comparison between corresponding bands. In Table I the wave-lengths and absorption coefficients of the principal bands of these substances are tabulated.

Beer's law apparently holds throughout the visible region for these substances since absorption coefficients for different solution concentrations at the same wave-length agree very well.

<sup>6</sup> Kirstahler, Tab. Biol. Period. 1, 258 (1931).