

## THE SPECTROSCOPY OF THE PORPHYRINS

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## 1. INTRODUCTION

THE spectroscopy of the porphyrins is one of the existing branches of molecular physics in which interest has been steadily increasing. Molecules of porphin derivatives contain macrocyclic conjugated systems with a large number of  $\pi$ -electrons, characterized by the presence of branching and heteroatoms in the conjugated chains; the molecules can have equilibrium configurations of high symmetry. All this gives interest and importance to the study of the physicochemical properties of the porphyrins. However, the spectroscopic study of the porphyrins is important not only in the value of the obtained information in conjunction with topics of spectroscopy and chemical structure of polyatomic molecules, but also in that this field is closely related to topics of biochemistry, and above all, to photosynthesis.

As K. A. Timiryazev expressed it, photosynthesis is, in the final analysis, the process on which all manifestations of life on the earth depend. The problem of photosynthesis is now attracting more and more attention from specialists in various fields: biologists, biochemists, chemists, and physicists. Besides the obvious direct meaning which the solution of the photosynthesis problem would have for biology, in perspective, it could lead to results of great practical importance. Ever since the time of Timiryazev, scientists have dreamed of utilizing the vast amount of radiant energy transmitted by the sun to the earth by means of artificial photosynthesis. Such an industrial adaptation of the photosynthesis process, if carried out, could revolutionize energetics and the chemical industry. The words of one of the most important physicists of our century, F. Joliot-Curie, are to the point here: "While I too believe in the future of atomic energy, and am convinced of the importance of this discovery, however, I think that a real revolution in energetics will take place only when we can synthesize in bulk molecules analogous to chlorophyll, or even better. In order to achieve this goal, first of all we must study in detail this type of molecule and the act of photosynthesis."<sup>[1]</sup>

The first step of photosynthesis in a plant is undoubtedly the absorption of a light quantum by the  $\pi$ -electrons of a chlorophyll molecule. Hence, systematic studies of the electronic structure of molecules of all classes of porphin derivatives, including chlorophyll, by various spectroscopic methods seems neces-

sary for a deep understanding of the nature of the optical excitation in photosynthesis and the subsequent fate of the absorbed light energy. Spectroscopy is especially appropriate here, since it deals directly with the excited electronic states of the molecules. "One might say, as it were, without especially distorting the actual course of history," said S. I. Vavilov, "that the number and importance of new results in the field of study of photosynthesis increases in parallel with the application of more and more delicate physical, and especially optical, methods."<sup>[2]</sup>

While the spectroscopic properties of chlorophyll must be directly related to its biological function, there is no such direct relation for the other porphin derivatives playing roles in important biological processes (e.g., hemoglobin). However, even here spectroscopic studies must lead to a deeper understanding of the important properties of these compounds.

This article will attempt to review as completely as possible the studies on the spectroscopy of the porphyrins. In presenting this material, the authors have tried to give from a unified viewpoint the concrete results achieved, and to point out the yet unsolved problems.

## 2. A BRIEF OUTLINE OF THE CHEMICAL STRUCTURE OF PORPHYRIN MOLECULES

The prototype of the porphyrin series is porphin, whose molecule contains four pyrrole rings joined by methine bridges in an overall conjugated system (Fig. 1). In the structural formula of a porphyrin (Fig. 1a), two double bonds are not included in the conjugated system (Fig. 1b) according to the formal rules of alternation of single and double bonds. These bonds have been called "semi-isolated,"<sup>[3]</sup> since it is obvious that the wave-functions of their  $\pi$ -electrons must over-

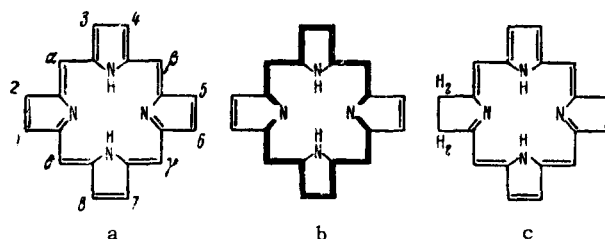


FIG. 1. Structure of the porphin ring. a) The porphin molecule; b) the conjugated bond system of porphin; c) the chlorin molecule.

lap with the wave-functions of the  $\pi$ -electrons of the ring.

The class of porphyrins may be divided into the porphyrins proper, the dihydroporphyrins [or chlorins (Fig. 1c)], and tetrahydroporphyrins (or bacteriochlorins). The porphyrins proper differ from porphin only in having side-chain substituents on the outer positions of the pyrrole rings or on the methine bridges, but do not differ in the structure of the conjugated bond system. In the molecules of the dihydroporphyrins, one of the "semi-isolated" double bonds is hydrogenated. That is, it is completely excluded from the conjugated system. In the molecules of the tetrahydroporphyrins, both "semi-isolated" bonds are hydrogenated.\*

The existing terminology, as we see, is not completely satisfactory, since the word porphyrin can have two meanings, general and particular. To avoid misunderstanding, we shall use below, as a rule, the term porphyrin to denote a non-hydrogenated derivative of porphin.

We can also distinguish as separate types of compounds the azaporphyrins, benzoporphyrins, and benzozaporphyrins. In the azaporphyrin molecules, one or several of the CH groups of the methine bridges are replaced by tertiary nitrogen atoms. Evidently, this replacement does not interfere with the alternation of single and double bonds. However, the geometry of the molecule, as it were, should change somewhat, since the angle between  $\sigma$ -bonds of nitrogen differs appreciably from that between the  $\sigma$ -bonds of carbon (the theoretical values are  $90^\circ$  and  $120^\circ$ , respectively). In benzoporphyrin molecules, benzene rings are fused to the pyrrole rings, and are apparently included in the overall conjugated system.† We should note that tetrabenzotetrazaporphyrin is called phthalocyanine; phthalocyanine and many of its metal derivatives are widely used in industry as very fast pigments.

The set of substituents found in the porphyrins is rather limited: the groups  $\text{CH}_3$  (methyl),  $\text{CH}_2\text{CH}_3$  (ethyl),  $\text{CH}=\text{CH}_2$  (vinyl),  $\text{COOH}$  (carboxyl),  $\text{CH}_2\text{CH}_2\text{COOH}$  (the propionic-acid residue), and a few others. The substituents can occupy either the positions 1–8, or the positions  $\alpha$ – $\delta$  (more rarely) (Fig. 1). N-methylporphyrin<sup>[6]</sup> has also been synthesized; in this molecule the methyl group is attached to one of the nitrogen atoms, and is located near the center of the porphin system. The best-known porphyrins have the following substituents:

\*There are references in the literature<sup>[4]</sup> to the possibility of preparing hexahydroporphyrins, in which one of the lateral double bonds is also hydrogenated. In such a case, the conjugated system is closed through an imine nitrogen atom.

†Recently Kuhn<sup>[5]</sup> has expressed a different viewpoint, according to which the bonds 1–2, 3–4, etc., of the pyrrole rings, when fused into the benzene rings, are incorporated into the independent conjugated systems of the latter, and act as though isolated from the overall conjugated system, which then consists of only the inner 16-membered ring.

etioporphyrin:  $4\text{CH}_3, 4\text{CH}_2\text{CH}_3$ ;  
 mesoporphyrin:  $4\text{CH}_3, 2\text{CH}_2\text{CH}_3, 2\text{CH}_2\text{CH}_2\text{COOH}$ ;  
 protoporphyrin:  $4\text{CH}_3, 2\text{CH}=\text{CH}_2, 2\text{CH}_2\text{CH}_2\text{COOH}$ ;  
 deuteroporphyrin:  $2\text{H}, 4\text{CH}_3, 2\text{CH}_2\text{CH}_2\text{COOH}$ ;  
 coproporphyrin:  $4\text{CH}_3, 4\text{CH}_2\text{CH}_2\text{COOH}$ ;  
 pyrroporphyrin:  $1\text{H}, 4\text{CH}_3, 2\text{CH}_2\text{CH}_3, 1\text{CH}_2\text{CH}_2\text{COOH}$ ;  
 phylloporphyrin:  $1\text{H}, 4\text{CH}_3, 2\text{CH}_2\text{CH}_3, 1\text{CH}_2\text{CH}_2\text{COOH},$   
 $1\text{CH}_3 (\alpha-\delta)$ ;  
 rhodoporphyrin:  $4\text{CH}_3, 2\text{CH}_2\text{CH}_3, 1\text{COOH},$   
 $1\text{CH}_2\text{CH}_2\text{COOH}$ ;  
 tetraphenylporphin:  $4\text{C}_6\text{H}_5 (\alpha-\delta)$ .

Most of the porphyrins can have isomeric forms differing in the relative arrangement of the substituents.<sup>[7]</sup> Four isomers are possible for etioporphyrin, fifteen for protoporphyrin, and twenty-one for rhodoporphyrin. The type of isomer is denoted by a Roman numeral, e.g., etioporphyrin II. Interestingly, while one can prepare synthetically all of the isomers, only certain definite forms are found in nature. Thus, the heme of the blood is always a derivative (a complex with ferrous iron) of protoporphyrin IX. Thus, all porphyrins derived from natural hematin compounds belong to type IX. The isomeric porphyrins differ very slightly in their physicochemical properties.

In acid media, porphyrin molecules take up two protons, forming doubly-charged positive ions. On the other hand, a porphyrin molecule can give up its central protons and take up a metal atom. This dual (amphoteric) nature of the porphin ring is due to the presence of unshared electron pairs on two of the central nitrogen atoms. In an acid medium, these nitrogen atoms take up protons (the unshared pairs becoming shared in the N-H bonds), while in reacting with a metal, the electrons of the unshared pair stabilize the complex compound by participating in the bond to the metal. In both cases, a donor-acceptor bond is formed.

The porphyrins containing carboxyl groups have acid properties, and are soluble in aqueous alkalis. These groups can be easily esterified, the porphyrin esters thus obtained being insoluble in water. The porphyrin esters and the carboxyl-free porphyrins have weakly basic properties, whence they are often referred to as the "free bases," in distinction from the metalloporphyrins.

The chlorins (dihydroporphyrins) differ appreciably in their physicochemical properties from the porphyrins; they are less stable, and more prone to undergo photochemical reactions. The side-chain substituents in the molecules of the chlorins are the same as in the porphyrins. Isomerism is likewise possible here.

The most important representative of the class of metallochlorins is the green photosynthetic pigment of the leaves of plants, chlorophyll. In addition to the hydrogenated double bond, the chlorophyll molecule has another essential structural peculiarity, a cyclopentane ring fused to the conjugated system. Notably, the porphyrins containing this ring (close relatives of

chlorophyll) differ somewhat in their properties from the other porphyrins.

In bacterial photosynthesis, the role of photosensitizer is played by bacteriochlorophyll, the magnesium complex of a tetrahydroporphyrin with hydrogenated pyrrole rings in opposite positions, and with a system of side-chain substituents similar to that of chlorophyll. The derivatives of tetrahydroporphyrin with opposite rings hydrogenated are therefore called bacteriochlorins. Tetrahydroporphyrins have also been described<sup>[4,8]</sup> having the hydrogenated pyrrole rings in adjacent positions.

More detailed information on the structure of porphyrin molecules, as obtained by spectroscopic methods,<sup>[13]</sup> is given in the following sections.

### 3. INFRARED SPECTRA OF THE PORPHYRINS AND SOME PROBLEMS OF MOLECULAR STRUCTURE

The study of the infrared spectra of organic compounds permits us to get important information on the structure and optical properties of molecules. At the same time, the application of infrared spectroscopic methods to very complex molecules often provides very limited information. Above all, this involves the difficulties of interpreting the spectra. Only the comparison of a large number of related compounds with regularly-varying structures makes it possible for us to solve this problem at all. From this standpoint, the porphyrins are very difficult compounds. Only the high symmetry of the structure of these molecules lets us hope to apply successfully infrared spectroscopic methods to these interesting compounds. At present there is a relatively large amount of information on the infrared spectra of the porphyrins. However, most of the studies have been intended to solve narrow problems involving the biological or photochemical functions of these compounds. We must note that in many cases the results of studies of the infrared spectra do not agree, but sometimes directly contradict one another. A number of infrared spectroscopic studies of the porphyrins, mainly chlorophyll,<sup>[9-10]</sup> are concerned with the keto-enol equilibrium under varying conditions. This problem is of special interest, and is outside the limits of this review.

The first information on the infrared spectra of porphin-type compounds was published in 1933 by Stair and Coblentz.<sup>[11]</sup> By careful measurements, these authors obtained infrared spectra of chlorophylls a and b, ethylchlorophyllide, pheophytin, phytol, made a comparison of these spectra, and interpreted certain bands. Since then, great advances have been made, both in the scope of possibilities for spectroscopic study, and in porphyrin chemistry. At the same time, the experiments of Weigl and Livingston<sup>[12]</sup> on the same compounds twenty years later gave no new results, but completely confirmed the data of the original authors.

Since the fundamental aim of this article is to examine the results of the spectroscopic study of the porphyrins, it seems convenient to take up only the general problems of the structure of these molecules and allied fields, and not go into details involving the participation of molecules of this class in biochemical processes. Thus we shall discuss only those results which are of interest from the standpoint of modern concepts of the structure of porphyrin molecules.

In principle, the central hydrogen atoms in porphyrin molecules can be in adjacent or opposite positions. The symmetry of the molecule depends on the arrangement of these atoms. X-ray diffraction data<sup>[13]</sup> do not permit us to determine the positions of the hydrogen atoms, or provide sufficient grounds for assigning neutral porphyrin molecules to definite symmetry groups. On the other hand, such an assignment is quite necessary for reliable interpretation of the electronic spectra of this class of compounds. The molecular symmetry  $D_{2h}$  corresponds to opposite positions of the central hydrogen atoms, and the symmetry  $C_{2v}$  to adjacent positions. A difference in the structure of the central part of the molecule involving a change in the symmetry of the molecular structure must affect the infrared spectra. In fact, group theory predicts five absorption bands corresponding to N-H vibrations in the spectra of porphyrins if the symmetry of the molecule is  $C_{2v}$ , but only three if the symmetry is  $D_{2h}$ . The spectra of the porphyrins are rather complex, and their interpretation is far from complete at present. Hence, Mason<sup>[14]</sup> had to study carefully the infrared spectra of ordinary and N-deuterated (with the central hydrogen atoms replaced by deuterium) porphyrins in order to determine the number of N-H vibration bands. A comparison of the spectra showed that there are three bands corresponding to N-H vibrations for the porphyrins proper, but five for the chlorins. Thus, if the assignment of the bands is correct, the porphyrins in neutral media have symmetry  $D_{2h}$ , and the chlorins  $C_{2v}$ . Hence it directly follows that the hydrogen atoms in porphyrin molecules are located opposite one another. We cannot draw such an unequivocal conclusion regarding the chlorins. The problem is that the chlorins have a rather low symmetry, either when the hydrogen atoms are opposite ( $C_{2v}$ ), or when they are adjacent ( $C_s$ ). The loss of symmetry here is primarily due to the hydrogenation of the lateral double bond. Besides, we can hardly expect that the hydrogenation of the lateral bond would bring about a rearrangement of the central hydrogen atoms. Probably, the chlorins also have the central hydrogen atoms in opposite positions.

The low symmetry of the neutral porphin molecule results in other peculiarities in the infrared spectra. Since the symmetry of a porphyrin molecule in neutral medium is  $D_{2h}$ , the pyrrole rings in the molecule are not equivalent. Furthermore, in the case of phthalocyanine we can hardly expect even the benzene rings to

be equivalent. Thus the frequencies of corresponding vibrations of groups of atoms contained in different pyrrole rings will not be equal. These frequencies must become equal in the metalloporphyrins, in which the pyrrole rings are equivalent, as will be shown below (Sec.6). A thorough comparison of the spectra of many porphyrins (of point-group symmetry  $D_{2h}$ ) and their metal derivatives has actually shown that the infrared spectrum becomes sparser in going from the neutral porphyrin to its metal derivatives.<sup>[15,16]</sup> Unfortunately, the infrared spectra of all porphyrins and phthalocyanines are rather complex, and it is difficult to speak of concrete frequencies in most cases.

The presence of two N-H groups and two tertiary nitrogen atoms in the center of the free porphyrin molecule permits us to assume that intramolecular N-H...N hydrogen bonds can be formed. Indeed, the position of the absorption band for N-H stretching vibrations differs markedly from the position of the corresponding band in the spectrum of pyrrole. On this basis, many researchers consider the existence of an intramolecular hydrogen bond to be an established fact.<sup>[14,17-19]</sup> In the opinion of some authors,<sup>[17]</sup> this hypothesis is confirmed by the results of an x-ray diffraction analysis<sup>[13]</sup> showing that the phthalocyanine molecule is somewhat elongated in the direction of the line joining the hydrogen atoms. The hypothesis asserting the existence of intramolecular hydrogen bonds, while reasonable, is not yet proven, and has a number of vulnerable points.

We shall take up in further detail the experimental facts relating to this problem. The absorption band of pyrrole corresponding to N-H stretching vibrations occurs at  $3495\text{ cm}^{-1}$ . In addition, there is a broad band with a maximum at  $3410\text{ cm}^{-1}$ , with a large half-width and an intensity depending on the external conditions (temperature, solvent). This band is interpreted as the stretching vibration of N-H bonds taking part in intermolecular hydrogen bonds.<sup>[20]</sup> When the molecule becomes more complex, in particular, on going to indole and then to carbazole, the unbound N-H band is shifted first by  $10\text{ cm}^{-1}$ , and then again by  $10\text{ cm}^{-1}$  to lower frequencies.<sup>[21]</sup> The replacement of the hydrogen atoms by more active groups leads to a further shift in this band. Thus, in pyrrolealdehyde the corresponding absorption band is found at  $3465\text{ cm}^{-1}$ , in 2, 3, 4-trimethyl-5-carbomethoxypyrrole at  $3465$  and  $3480\text{ cm}^{-1}$ , in 3, 4, 5, 3', 4', 5'-hexamethylpyrromethane at  $3455\text{ cm}^{-1}$ , in bilirubin at  $3410\text{ cm}^{-1}$ .<sup>[15]</sup> Thus, as the molecule becomes more complex, even without incorporation of the pyrrole rings into a macrocycle, the N-H band is shifted by  $100\text{ cm}^{-1}$ . There is a further shift in this band in going to the porphyrins. In porphin it is found at  $3305\text{ cm}^{-1}$ , in tetraphenylporphin at  $3315\text{ cm}^{-1}$ , in tetrazaporphin at  $3300\text{ cm}^{-1}$ , in meso-porphyrin at  $3315\text{ cm}^{-1}$ , and in phthalocyanine at  $3290\text{ cm}^{-1}$ . The given facts indicate a regular shift in the band as the molecule becomes more complex.

Hence, the shift in the absorption band of the N-H group is not itself sufficient for us to consider the presence of an intramolecular hydrogen bond in porphyrin molecules to be established. A study of the frequencies of the N-H deformation vibrations shows that the incorporation of the pyrrole rings into the porphin ring is accompanied by a shift in the absorption bands corresponding to the out-of-plane vibrations by about  $100\text{--}150\text{ cm}^{-1}$  to higher frequencies, and a shift to lower frequencies of the bands corresponding to in-plane deformation vibrations (by about the same amount). Such shifts in the frequencies of the deformation vibrations are characteristic of the effect of conjugation on infrared spectra. On the contrary, the participation of an N-H group in a hydrogen bond lowers the out-of-plane deformation frequencies.<sup>[22]</sup> We must note that not only the N-H bands shift as the pyrrole rings are incorporated in the porphyrin ring. The C-H deformation vibrations of the pyrrole rings behave just like the N-H vibrations, although the effect is somewhat less marked.<sup>[15]</sup> Thus, the fundamental experimental fact responsible for the widespread acceptance of the hypothesis of intramolecular hydrogen bonds in the molecules cannot be considered a sufficient argument for this view. All the facts known at present can be successfully explained, on the one hand, by the influence of conjugation on the infrared spectra of the porphyrins, and on the other, by the change in the force constants and angles owing to deformation of the pyrrole rings in forming the macrocycle. On the basis of the existing information, it is hard to decide which of these factors we should give preference to. Probably the latter factor plays a larger role than the former, since the introduction of a metal atom into the center of the molecule, which involves considerable changes in the conjugated bond system, results in insignificant shifts in the C-H bands, their positions depending slightly on the nature of the metal (the shifts are about  $20\text{ cm}^{-1}$ <sup>[23]</sup>). The x-ray diffraction results mentioned above can be satisfactorily explained by the repulsion of the central hydrogen atoms, which unavoidably entails a certain deformation of the entire molecule. We should note that Donohue<sup>[24]</sup> considers that the formation of an intramolecular hydrogen bond in the porphin ring is not favored by stereochemical considerations.

In discussing the problem of the possible existence of intramolecular hydrogen bonds in porphyrin and phthalocyanine molecules, it is pertinent to note an assumption which has been made in the study of the infrared spectra of various crystalline modifications of phthalocyanine. Here, it is sometimes assumed<sup>[25]</sup> that the small differences in the position of the N-H stretching absorption band between the  $\alpha$ - and  $\beta$ -modifications of phthalocyanine arise from differing energies of intermolecular hydrogen bonds involving the central hydrogen atoms.

A considerable number of studies on the infrared spectra of the porphyrins have been concerned with tetraphenylporphin. The most interesting problem which appears in the study of this compound is the effect of the benzene rings on the  $\pi$ -electron porphyrin bond system. On the one hand, it is quite natural to assume that the benzene rings are included in the conjugated bond system of the porphin ring, but on the other hand, there are experimental data<sup>[26]</sup> contradicting this assumption to some extent, and in a way indicating the absence of such a conjugation.

The fundamental experimental grounds suggesting that the benzene rings are included in the conjugated system of the porphin ring are the following. First, there are some rather firm criteria permitting the distinction of a benzene ring with external conjugation from a benzene ring without conjugated substituents. These involve the spectral range 1500–1600  $\text{cm}^{-1}$ .<sup>[22]</sup> The infrared spectrum of tetraphenylporphin in this range shows the presence of conjugation. Second, the introduction of a metal atom into the center of the molecule is accompanied by considerable changes in the infrared spectra of the benzene rings.<sup>[15,23]</sup> These changes, which amount to shifts and changes in intensity of many absorption bands, even involve the vibrations of the C-H groups, which are very characteristic, as is known. Third, there is also a reverse effect: the introduction of various substituents on the benzene rings of tetraphenylporphin leads to a shift in the N-H absorption bands.<sup>[26]</sup> Finally, the electronic absorption and luminescence spectra are strongly shifted to longer wavelengths with respect to the corresponding spectra of porphin, although these molecules differ only in the benzene rings. The red shift of the long-wavelength absorption band of more than 800  $\text{cm}^{-1}$  can be explained by assuming conjugation of the benzene rings with the porphyrin ring. As is known, such a considerable extension of the conjugated bond system can lead to such a spectral shift.<sup>[27]</sup> Analogous phenomena are observed in going from azaporphin to phthalocyanine. Here the shift is even greater (about 2000  $\text{cm}^{-1}$ ).

The basic argument against this hypothesis is the low sensitivity of the electronic absorption spectra of tetraphenylporphin to replacement of the hydrogen atoms of the benzene rings by various substituents (Cl,  $\text{NO}_2$ , etc.), which alter the electron-density distribution in the conjugated bond system.<sup>[26]</sup> This fact probably indicates that the effect of these substitutions is not very great, and is fundamentally limited to the redistribution of the electron density within each benzene ring alone. As a compromise conclusion from all these experimental data, obviously, we could state that the benzene rings in the molecules of tetraphenylporphin enter into conjugation with the porphin moiety of the molecule, at least partially.

In studying the infrared spectra of the porphyrins and especially the phthalocyanines, considerable atten-

tion is commonly paid to another type of interaction with other kinds of molecules. While these very interesting studies, which have been successfully carried out by Terenin and his students,<sup>[25,28]</sup> are outside the limits of this review, the basic results can prove useful in discussing certain results of the study of the effect of pH on the electronic spectra of the porphyrins, and thus it is pertinent to cite them here.

These authors studied the electronic and vibrational spectra of sublimed films of phthalocyanine and its metal derivatives, and also films of these compounds treated with gaseous HCl,  $\text{CH}_3\text{COOH}$ , and HBr. From these studies, they concluded<sup>[28]</sup> that the phthalocyanines under these conditions undergo ionic bonding of  $\text{H}^+$  to the nitrogen atoms of the phthalocyanine molecule. A comparison with the data of other authors<sup>[29]</sup> on the effect of pH on the electronic spectra of the phthalocyanines in solution, and also chlorophyll,<sup>[30]</sup> permitted them to conclude that in phthalocyanine molecules, protons can be bound not only to the nitrogen atoms of the pyrrole rings, but also to the nitrogen atoms linking the pyrrole rings in the molecule. The question whether protons can bind to the bridge nitrogen atoms is of fundamental significance for a correct understanding of the spectral regularities of molecules of the porphin series (especially the azaporphyrins). Hence, a further experimental and theoretical study of this problem is very desirable.

#### 4. ELECTRONIC SPECTRA OF THE PORPHYRINS

a) Absorption spectra and their relation to the molecular structure. The characteristic absorption spectra of the porphyrins in the visible attracted the attention of the very first researchers. However, spectroscopy was originally used only for analytical purposes (to check for completion of reactions, to test the purity of products, etc.). In the Twenties, papers began to appear on the quantitative study of the spectroscopic regularities of the porphyrins. We must note the studies of Conant and Kamerling,<sup>[31]</sup> Hellström,<sup>[32-35]</sup> Haurowitz,<sup>[36-37]</sup> and especially the studies of Stern and his associates, who obtained precise quantitative data for a very large number of compounds.<sup>[38-47]</sup> Interesting studies of the spectroscopic and photochemical properties of tetraphenylporphin and its derivatives have been conducted in the post-war period by Calvin, Dorough, et al.<sup>[4,45-46]</sup>

The absorption spectra of porphyrins in the visible show four weak, relatively narrow bands separated by approximately equal intervals. At the boundary between the ultraviolet and the visible, the porphyrins show a very intense narrow band, commonly called the Soret band. According to Stern,<sup>[38]</sup> the bands in the visible are designated by Roman numerals, beginning on the long-wavelength side. In some porphyrins, a narrow band denoted as Ia appears between bands I and II.

The absorption bands of porphyrins having different substituents show different relative intensities. A detailed study of the absorption spectra of the porphyrins led Stern to the conclusion that among the porphyrins, out of the 24 possible types of intensity distribution in the four-banded spectra, only three spectral types are observed: the "etio-type" (IV, III, II, I), the "rhodo-type" (III, IV, II, I), and the "phyllo-type" (IV, II, III, I)\*. [41] The spectra of etioporphyrin, rhodoporphyrin, and phylloporphyrin, as characteristic representatives of these types, are shown in Fig. 2.

Stern was able to relate these "spectral types" to the properties of the side-chain substituents in the molecule (see [7]). The most widespread etio type is found in porphyrins having simple alkyl substituents in the free positions (1-8) on the pyrrole rings. Such groups as, e.g., the propionic-acid residue  $\text{CH}_2\text{CH}_2\text{COOH}$  can be treated as alkyl substituents in their influence on the conjugated bond system, since the double bonds which they contain are isolated from the conjugated bond system by a chain of single bonds.

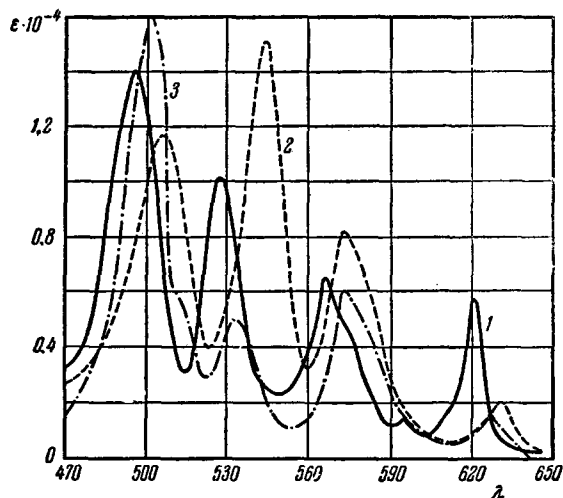


FIG. 2. Absorption spectra in dioxan:[7] 1—etioporphyrin; 2—rhodoporphyrin; 3—phylloporphyrin.

The introduction of unsaturated vinyl groups does not alter the etio type, although it shifts the spectrum appreciably to longer wavelengths. The symmetrically substituted  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ -tetraphenylporphin also has a spectrum of the etio-type.

The rhodo type occurs in compounds having a carbonyl group CO directly conjugated with the porphin ring. In the porphyrins containing two carbonyl groups, the rhodo type is enhanced if they occur on opposite

pyrrole rings, and weakened (going over to etio type) if they occur on adjacent pyrrole rings. Notably, the enhancement of the III band on introduction of the second carbonyl group is accompanied by a shift in this band to longer wavelengths. Here band II seems to be strengthened, owing to increased overlap with the III band, and the spectral type (III, II, IV, I) does not correspond formally to the rhodo type. An analogous form is shown by the spectra of the porphyrins related to chlorophyll, in which the carbonyl group is contained in a cyclopentane ring.\*

The introduction of an alkyl group into one of the positions  $\alpha$ ,  $\beta$ ,  $\gamma$ , or  $\delta$  results in the phyllo type. If in addition there is a carbonyl group, the two effects compensate one another, and we get the etio type. The phyllo type is also observed in porphyrins containing carbocyclic rings without carbonyl groups (certain derivatives of chlorophyll).

The observance of the stated empirical rules makes it interesting that the spectrum of porphin itself, which has no side-chain substituents, belongs to the phyllo type. This fact has been checked by a number of investigators, and can be considered as firmly established. [49,50] The introduction of two alkyl substituents, or even four (on adjacent pyrrole rings), does not affect the phyllo type. Four alkyl substituents situated in pairs on opposite pyrrole rings give the etio type. On the basis of these data, statements have often been made in the literature about the "anomaly" of porphin (see, e.g., [51]), since we might naturally expect porphin to have the etio type characteristic of the symmetrically-substituted porphyrins without carbonyl groups,  $\gamma$ -substituents, or carbocyclic rings. The reason for this apparent anomaly will be discussed in Sec. 7.

A very important characteristic of the porphyrin ring is that the absorption spectrum becomes simpler upon introduction of a metal atom or two extra protons (in forming the dication in acid media) (Fig. 3). This spectroscopic regularity appears in all compounds not having hydrogenated pyrrole rings, including the aza- and benzoporphyrins. In particular, in the porphyrins proper, regardless of the spectral type, the four-banded spectrum becomes two-banded, and the Soret band is narrowed. Spectral band I in acid media is shifted to shorter wavelengths by about 25  $\text{m}\mu$ , as compared with band I in neutral media (with an order of intensities II, I). In the spectrum of porphin in acid media, the band I is so weak that the spectrum seems single-banded. [40] The spectra of the metalloporphyrins are shifted further to shorter wavelengths, and show a different order of band intensities (ordinarily I, II).

Large changes in the spectra of the porphyrins are

\*The numbers in parentheses indicate the order of intensities of the absorption bands, beginning with the strongest. Spectral types (I, II, III, IV), or (I, II, IV, III), etc., are possible. The total number of these is equal to the number of permutations of four elements, or 24.

\*Recently Lemberg and Falk suggested distinguishing the spectra of these compounds as a special type, the oxorhodo type (from the name of the typical representative, oxorhodoporphyrin). [46]

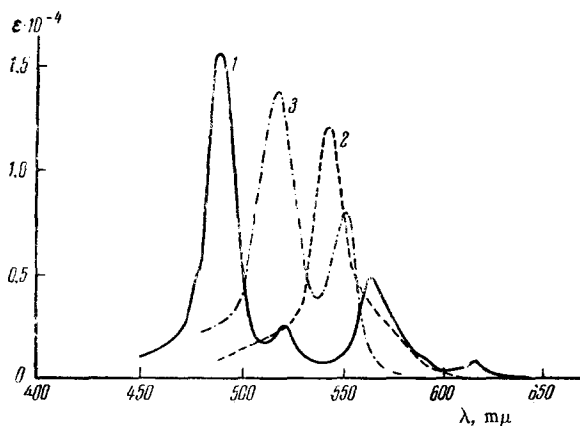


FIG. 3. Absorption spectra of porphin:<sup>[50,40,42]</sup> 1 – in neutral medium; 2 – in acid medium; 3 – Cu-porphin.

also observed upon hydrogenation of the pyrrole rings (on going over from the porphyrins to the chlorins). The characteristic peculiarity of the spectra of the chlorins (Fig. 4) is the high intensity of the long-wavelength absorption band. This band is ordinarily shifted by 10–20 m $\mu$  to longer wavelengths with respect to the corresponding porphyrin. Interestingly, spectral bands III and IV of the porphyrins are hardly shifted, and do not change in intensity upon hydrogenation of the double bond in one of the pyrrole rings. The Soret band in the chlorins is appreciably broadened. The introduction of a metal atom into the molecule somewhat shifts the long-wavelength absorption band to shorter wavelengths, and in a number of cases it is appreciably strengthened. The introduction of a metal has an especially marked effect on the order of intensities of the weak “porphyrin” absorption bands in the yellow-green region.

The derivatives of tetrahydroporphin with opposite pyrrole rings hydrogenated (the bacteriochlorins) are characterized by a very intense absorption band in the near infrared (750–770 m $\mu$ ) (Fig. 5), and the Soret band is split into two components. Insertion of a metal into the center of a bacteriochlorin molecule has very little effect on the form of the spectrum. The tetra-

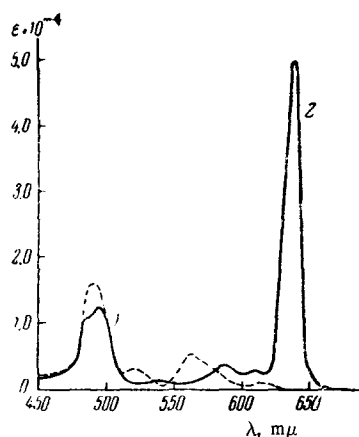


FIG. 4. Absorption spectra in benzene:<sup>[49,50]</sup> 1 – porphin; 2 – chlorin.

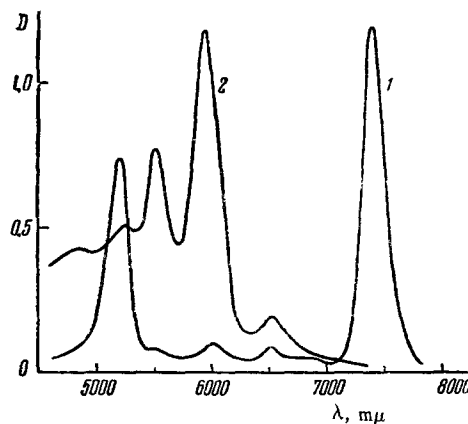


FIG. 5. Absorption spectra of tetraphenyltetrahydroporphin:<sup>[8]</sup> 1 – with hydrogenation of the double bonds in opposite positions; 2 – in adjacent positions.

hydroporphins having adjacent hydrogenated rings have spectra somewhat similar to those of the chlorins. The long-wavelength absorption band of these compounds is situated in the red region of the spectrum.<sup>[4]</sup>

An interesting effect on the spectra of the porphyrins is brought about by the substitution of a nitrogen atom for a methine group CH (Fig. 6). The electronegative nitrogen atoms strongly perturb the  $\pi$ -electron cloud. The result of one aza-substitution is an appreciable increase in the intensities of bands I and III, a weakening of bands II and IV, and a slight shift of band I to shorter wavelengths. An increase in the number of nitrogen atoms leads to a further increase in bands I and III, broadening and weakening of bands II and IV, and a small general red shift of the visible spectrum (band III is shifted more strongly).<sup>[52]</sup> The spectra of the metal derivatives of the azaporphyrins contain two bands in the visible, just like the ordinary metal-porphyrins. They differ in that band I is stronger in the former, analogously to bands I and III of the free azaporphyrins. The Soret band in the azaporphyrins and their metal derivatives is greatly broadened

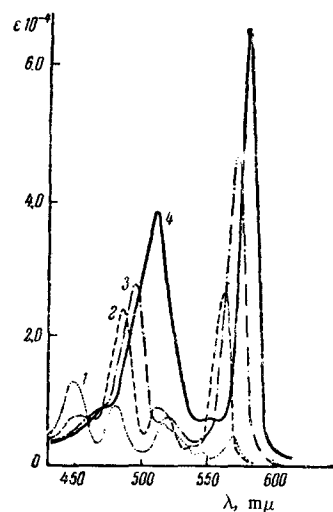


FIG. 6. The effect of aza-substitution on the absorption spectra of porphyrins.<sup>[52]</sup> 1 – Etioporphyrin; 2 – mono-azaetioporphyrin; 3 – diazaetioporphyrin; 4 – tetrazaetioporphyrin in dioxan.<sup>[52]</sup>

and shifted to shorter wavelengths. Here, this effect becomes more clearly marked as more nitrogen atoms are introduced.

Incorporation of benzene rings into the conjugated system strengthens the visible absorption bands, and shifts them to longer wavelengths. Analogously to tetrazaporphin, phthalocyanine and tetrabenzoporphin have two intense absorption bands in the visible, which merge into one band on introduction of a metal atom.

b) Mirror symmetry of the absorption and emission spectra. The absorption spectra of the porphyrins, even those published in the early studies, are quite reliable, and Stern's data can be used as a standard for identification of porphyrins. We cannot say the same of the fluorescence spectra. While the fluorescence spectra have been studied by many authors (Dh  r  , [53], Stern, [54,55] and others), the use of photographic methods without taking into account the spectral sensitivity of the photographic materials hinders the interpretation of the data.

The mirror-image similarity of the absorption and fluorescence spectra of the porphyrins was first noted by Hellstr  m, [32] who made purely qualitative comparisons of the two spectra by superimposing them in a spectroprojector. The mirror symmetry of the absorption and emission spectra of tetraphenylporphin were noted in a study by Weigl, [56] who recorded the fluorescence spectrum photoelectrically. However, in a number of cases among the metalloporphyrins, the literature data indicate a violation of the mirror-symmetry rule. Thus, for example, according to the data of Dorough et al [46,57] Zn-tetraphenylporphin has two sharp absorption bands (at 595 and 555 m $\mu$ ) and one broad emission band at about 650 m $\mu$ . Since obedience to the mirror-symmetry rule is of great importance in the interpretation of the electronic spectra, a special study has been conducted of the mirror symmetry of the absorption and emission spectra of various porphyrins under various conditions. [16,58]

The rule of mirror symmetry of the absorption and emission spectra was stated by Levshin, [59] who also formulated the conditions for conformance to this rule. He showed that exact mirror symmetry of the spectra can occur when the following conditions are satisfied. First, the vibration frequencies manifested in the spectrum must be the same for the ground and excited states. Second, the matrix element of the dipole moment of the electronic-vibrational transition must not depend on whether the vibration is combined with the ground or the excited state. Third, the distribution function over the vibrational states must be the same for the ground and excited states. Numerous experimental studies of the luminescence of organic compounds have shown that the mirror-symmetry rule is rarely strictly obeyed, but the deviations are commonly small. [59] The existence of even approximate mirror symmetry and the nature of the deviations from strict mirror symmetry permit us to arrive at definite conclusions on the characteristics of the optical transitions.

Measurements performed in a highly-sensitive photoelectric spectrometer have shown that all of the studied porphyrins obey the mirror-symmetry rule, but not strictly. In all cases the fluorescence spectra show two bands related by mirror symmetry to the two absorption bands at longer wavelengths. We must note that the fluorescence spectra of the metalloporphyrins, just like the free porphyrins, are independent of the wavelength of excitation.

The results of the measurements for a number of compounds are given in Figs. 7 and 8. In accordance with theory, [60,61] the spectra are plotted on a frequency scale, with the values of  $\epsilon/\nu$  and  $J_\nu/\nu^4$  plotted as ordinates.

We see from these diagrams that the mirror-symmetry rule holds rather well for the porphyrins. For the metal-free porphyrins in neutral media, the frequency condition is better satisfied, and the intensity condition more poorly. The latter fact can apparently be explained by the trivial effect of overlap of bands II and III in the absorption spectrum. Conversely, the metalloporphyrins obey the intensity condition well (for the two-banded absorption spectrum), but the frequency difference in the absorption spectrum is always less than in the emission spectrum. We must emphasize that Zn-tetraphenylporphin shows two fluorescence bands, at 608 and 660 m $\mu$ . Thus, some American authors [46,57] have noted the existence of only the second fluorescence band, which indicated an apparent violation of the mirror-symmetry rule.

An examination of the above-mentioned conditions

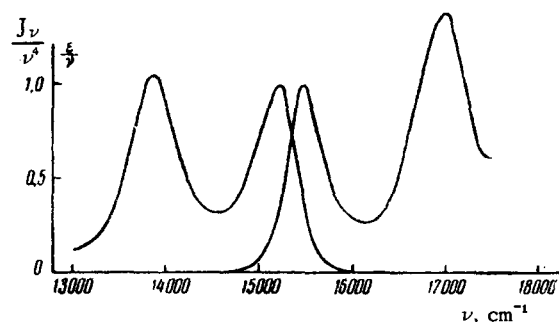


FIG. 7. Mirror symmetry of the absorption and emission spectra of tetraphenylporphin in isobutyl alcohol.

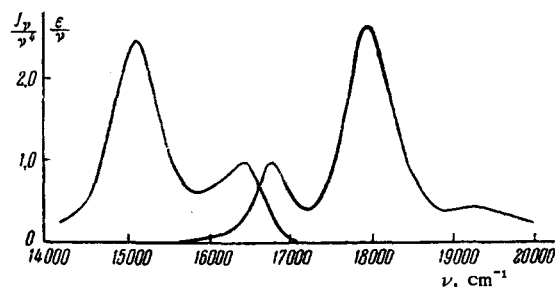


FIG. 8. Mirror symmetry of the absorption and emission spectra of Zn-tetraphenylporphin in isobutyl alcohol.



for mirror symmetry indicates that the mirror symmetry of the absorption and emission spectra arises from the fact that the absorption and emission bands belong to the same electronic transition, upon which vibrational structure is superimposed. Hence, the cited experimental data indicate that absorption bands I and II and the emission bands in the spectra of the porphyrins and metalloporphyrins belong to the vibrational structure of a single electronic transition. In principle, the mirror symmetry could arise from other causes, and the cited absorption and emission bands could belong to different electronic transitions. However, this situation is improbable, and has no analogy in the literature.

The frequency interval between the absorption bands of the metalloporphyrins is ordinarily about  $1200\text{ cm}^{-1}$ , which is appreciably less than the interval between bands I and II in the four-banded spectrum, which amounts to about  $1500\text{ cm}^{-1}$ . The latter frequency difference ( $1500\text{ cm}^{-1}$ ) appears also in the emission spectra of the metalloporphyrins, leading to a violation of the symmetry of frequencies. Since band II is due to the superimposition of vibrational structure, the decrease in the frequency interval in the absorption spectra of the metalloporphyrins can be explained by a decrease in the vibration frequencies manifested in the spectrum in the excited electronic state. Possibly, the metal atom exerts a weakening effect on the bond system of the porphin ring in the excited electronic state.

c) The effect of external factors on the electronic spectra. The properties of the surrounding medium show a weak influence on the positions of the energy levels of the porphin ring, and thus the opinion has been expressed that there is a sort of screening of the chromophoric groups. The shift in the spectral bands observed in going from one solvent to another or on changing the temperature through a rather wide range (from  $77^\circ$  to  $500^\circ\text{K}$ ) is ordinarily no more than  $5\text{ m}\mu$ , i.e., about  $200\text{ cm}^{-1}$ .

As compared with non-polar hexane, polar solvents and also benzene and dioxan shift absorption band I to shorter wavelengths, but band IV to longer wavelengths. This difference has been tentatively explained by a decrease in the vibrational frequencies in the excited state under the influence of the polar molecules.<sup>[37]</sup> Just as with the porphyrin spectra, the metalloporphyrin spectra are very insensitive to changes in the nature of the solvent. Exceptions occur in cases in which the solvent molecules can combine with the metal atom by a donor-acceptor bond owing to an unshared electron pair on the solvent molecule (e.g., pyridine<sup>[62]</sup>). The effect of complex formation with pyridine is especially large in the hematin (Fe-porphyrin) compounds.

Heating a porphyrin solution broadens the bands and shifts them to longer wavelengths. On lowering the temperature, a blue shift and narrowing of the bands are observed.

At liquid-oxygen temperature, the porphyrin bands become split, but here we must say that the data of different authors agree poorly with one another. For porphin, a very distinct splitting of band II and a less distinct splitting of the other bands have been described.<sup>[50]</sup> In the other porphyrins, the structure of band IV is best manifested, and III, II, and I more poorly.<sup>[31,63]</sup> References<sup>[31]</sup> and<sup>[63]</sup> disagree in the number of splitting components exhibited, but if we judge from the most intense components, we arrive at the following general picture: band IV splits into three components, band III into two, and bands II and I do not split. The commonly cited splitting has been ascribed to resolution of the vibrational structure of the electronic transitions. However, Dorough and Shen, who had found similar phenomena in tetraphenylporphin, ascribed them to a change in the equilibrium of isomers (or more exactly, tautomers) having adjacent and opposite arrangements of the hydrogen atoms; they based their argument on the fact that the effect is not observed in the metal derivatives.<sup>[57]</sup>

In the luminescence spectra at low temperatures, our measurements have shown that, in agreement with the observations of Dorough and Shen, splitting does not occur in the metal derivatives of tetraphenylporphin. However, the luminescence spectra of the metal derivatives of mesoporphyrin show a structure analogous to that of the spectra of the metal-free porphyrins (see also<sup>[64]</sup>). For these reasons, we can cast doubt on the conclusion that NH-isomers of the porphyrins exist, since the metal derivatives of mesoporphyrin cannot exhibit NH-isomerism, just as with the metal derivatives of tetraphenylporphin.

Recently Litvin and Personov<sup>[65]</sup> were able to obtain quasilinear luminescence spectra of phthalocyanine, Mg-phthalocyanine, and protoporphyrin in frozen normal paraffins (by the method of Shpol'skiĭ). Protoporphyrin, as well as the phthalocyanines, shows a qualitative mirror-image similarity of the absorption and emission spectra. These facts also indicate that the structure observed in the spectra of porphyrins at low temperatures is due to the resolution of the individual electronic-vibrational transitions. The frequency differences manifested in the spectra must be interpreted as the frequencies of the normal vibrations of the molecule in the ground state (for the emission spectra) or the excited state (for the absorption spectra).

d) The effect of the pH of the medium on the spectra of porphyrins. The pH of the medium shows a specific effect on the spectra of the porphyrins. This effect is considerably more marked than those of other factors. We shall discuss this problem in somewhat more detail.

As is known, a change in the hydrogen-ion activity in the solutions of various pigments has a considerable effect on the spectroscopic properties of the molecules in solution.<sup>[66]</sup> These changes in the absorption and

luminescence spectra are especially marked when the molecules in solution undergo ionization. A number of structural peculiarities of porphyrin molecules give rise to the very characteristic phenomena which appear in porphyrin solutions upon change in the pH of the medium.

First, in the porphyrins the nitrogen atoms capable of binding or releasing additional charges are situated in the center of a polyatomic molecule having a conjugated bond system of complex structure.

Second, the ionization of porphyrin molecules involves a radical change in the symmetry of the  $\pi$ -electron bond system of the molecules, as direct polarization experiments<sup>[67,68]</sup> indicate unequivocally (see Sec. 6).

Third, among the porphyrins, changes in the pH of the solution can in principle involve the formation of either singly or doubly charged ions.

These facts make studies of the effect of the hydrogen-ion concentration on the spectro-luminescent properties of the porphyrins quite essential for a proper understanding of the spectral regularities and for an elucidation of the peculiarities of the effect of the pH on the spectroscopic properties of this class of compounds. Porphyrin molecules in acid solutions ordinarily occur as doubly-charged ions. Here the two extra protons are located in the center of the molecule.

As polarization measurements indicate,<sup>[67,68]</sup> the excess charge is uniformly distributed throughout the  $\pi$ -electron bond system of the molecule. Under these conditions, the central nitrogen atoms become completely equivalent, while the symmetry of the molecule can be assigned to point group  $D_{4h}$ . Such a change in the structure of the conjugated bond system of the molecule is accompanied by specific changes in the absorption and luminescence spectra. As an example, Fig. 9 shows the absorption spectra of the dimethyl ester of protoporphyrin IX obtained from solutions with stepwise variation of pH.<sup>[69]</sup> Owing to the insolubility of the neutral porphyrin molecules in water, the measurements were made in non-aqueous solutions. Thus, strictly speaking, we cannot refer to the pH in the ordinary sense. However, there is a quite definite correlation between the spectra and the relative mass proportion of HCl added.

These data show isosbestic points, whose existence unambiguously indicates that equilibrium occurs between only two forms of absorbing centers in the solutions of varying pH.\* The four-banded spectrum belongs to the neutral porphyrin molecules, and the two-banded spectrum to porphyrin ions. Here the absorption spectrum of the ions is shifted to shorter wavelengths, whereas ordinarily the addition to molecules of excess charge not localized in any particular site results in an

\*The existence of these isosbestic points was apparently noted for the first time in reference<sup>[70]</sup>.

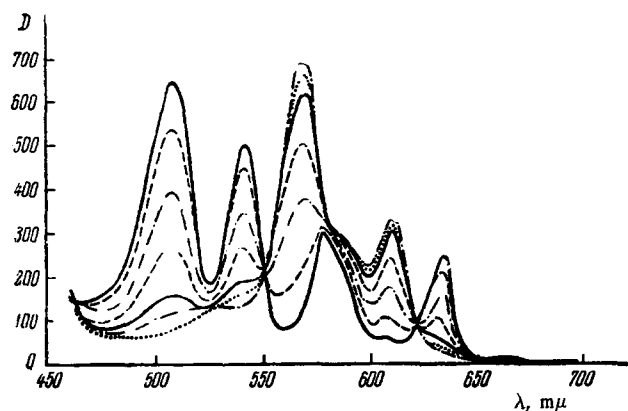


FIG. 9. Effect of acidity of the medium on the absorption spectra of protoporphyrin.

increase in the mobility of the  $\pi$ -electron cloud and a bathochromic effect in the spectra. This specific peculiarity of the porphyrins, as will be shown below (see Sec. 7), involves a change in the structure of the system of energy levels of the molecule, with degeneracy of the electronic states.

Thus, the results of a study of the absorption and luminescence spectra of solutions of porphyrins at different pH values, as well as the existing information on changes in the symmetry of the structure of the conjugated bond system of the porphyrin molecules, indicate that most porphyrins can exist either in the form of neutral molecules or of doubly-charged ions. The singly-charged ions of the porphyrins have lifetimes several orders of magnitude smaller than the doubly-charged ions, and are not manifested in the spectra. This peculiarity of porphyrin molecules of forming only doubly-charged ions obviously involves the equivalence of the central tertiary nitrogen atoms. In this regard we must note that there are statements in the literature that a singly-charged ion can exist in a porphyrin in which the equivalence of the pyrrole rings is highly perturbed.<sup>[71]</sup> As yet, this case remains an exception, and further study of this problem would be highly desirable.

Certain peculiarities in the effect of pH on the absorption spectra are observed in tetraphenylporphyrin.<sup>[72]</sup> In acid media the spectrum becomes single-banded (Fig. 10), and the long-wavelength band shows a high absorption coefficient. In addition, the presence of an isosbestic point indicates the equilibrium of only two forms in this case as well. Obviously, the peculiarities of tetraphenylporphyrin with regard to the effect of pH on the spectra involve the presence of the substituents on the methine bridges. Possibly they also involve the incorporation of the benzene rings in the conjugated system (see Sec. 3). However, there is no more definite information on this problem. A theoretical and experimental treatment of this problem would be very desirable.

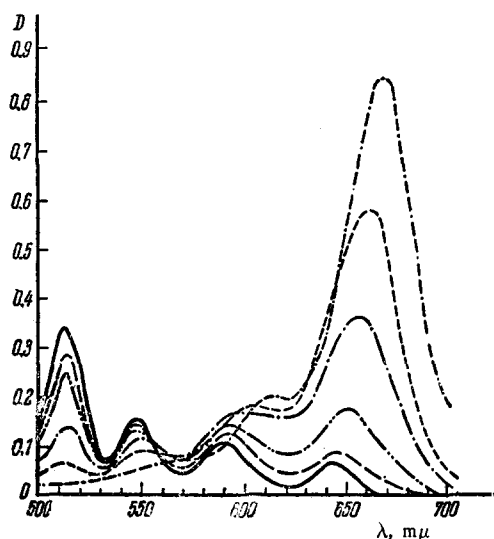


FIG. 10. Effect of the acidity of the medium on the absorption spectra of tetraphenylporphin.<sup>[3]</sup>

The situation is rather different in the effect of pH on the spectra of the chlorins. The marked violation of the equivalence of the pyrrole rings by the hydrogenation of one of the lateral double bonds makes possible the existence of both singly and doubly-charged ions.<sup>[73,69]</sup> This is manifested in the absorption spectra by a shift in the long-wavelength absorption band toward shorter wavelengths, first by a certain amount with an isosbestic point (to within a certain pH), and then by a different amount with a second isosbestic point (Fig. 11). The spectrum does not change appreciably in character. The blue shift in the spectrum, rather than red, as is usual, can be explained by the simultaneous action of two factors. On the one hand, a certain increase in the symmetry of the conjugated bond system must lead, as in the porphyrins, to an approach in the frequencies of the electronic transitions. On the other hand, an increase in the mobility of charges shifts the spectrum to longer wavelengths. The final result may be due to the predominance of the first factor.

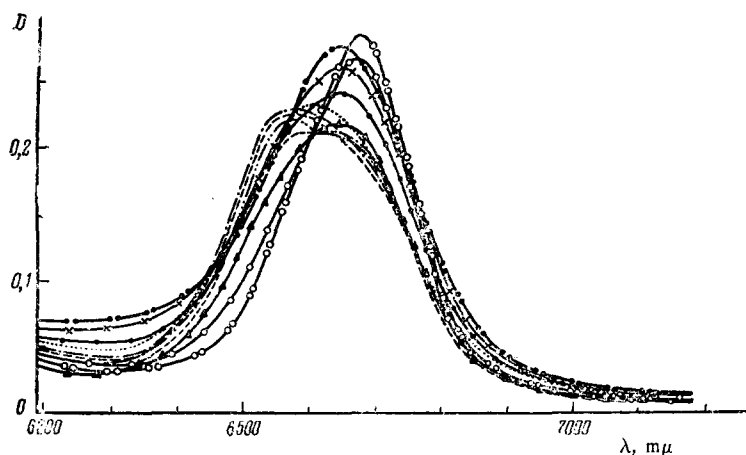


FIG. 11. Effect of the acidity of the medium on the absorption spectra of pheophytin.

e) The effect of the nature of the metal on the spectra of metalloporphyrins. As has been stated, the fluorescence spectra of luminescent metalloporphyrins show mirror symmetry with the absorption spectra. Hence, the changes in the luminescence spectra depending on the nature of the metal essentially copy the changes in the absorption spectra. Besides, many metalloporphyrins are not capable of luminescing. Hence, we shall deal in this section basically with the absorption spectra of the metalloporphyrins.

The electronic absorption spectra of the metalloporphyrins show two sharp, relatively weak bands in the visible and an intense Soret band, which is narrower than in the corresponding free porphyrins (Fig. 12). The general type of spectrum does not depend on the presence of side-chain substituents on the porphin ring. However, the characteristics of the latter affect the order of intensities and positions of the bands. Stern et al.<sup>[42]</sup> have made a study of the absorption spectra of the copper complexes of various porphyrins, and showed that the effect of side-chain substituents is appreciable only for band I, while band II is hardly altered in intensity, and follows band I at an approximately constant interval  $\Delta\nu = 1170-1220 \text{ cm}^{-1}$ . The behavior of band II in the two-banded spectrum is

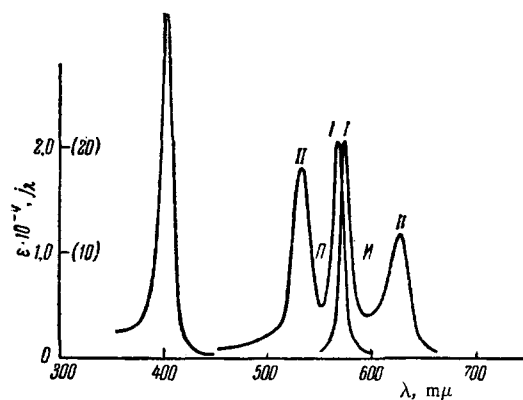


FIG. 12. Absorption and luminescence spectra of Zn-mesoporphyrin.

analogous to that of bands II and IV in the four-banded spectrum, as the latter are practically unchanged in intensity in going from one type of spectrum to another. In Cu-porphin, its di-substituted derivatives, and its tetra-substituted derivatives having substitution on adjacent pyrrole rings, band I is somewhat weaker than band II. For the other Cu-porphyrins containing side-chain substituents in the free positions of the pyrrole rings, including Cu-rhodoporphyrin, band I is stronger than band II. However, in the latter case, the presence of the carbonyl group results in a different value of  $\Delta\nu = 1425 \text{ cm}^{-1}$ .

Stern did not study the Cu-porphins substituted on the methine bridges. It has turned out that the absorption spectra of the copper complexes of  $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin<sup>[46]</sup> and  $\alpha, \beta, \gamma, \delta$ -tetramethylporphin<sup>[74]</sup> are of similar form, band I being very weak, in distinction from the complexes described above. The reason for the difference will be discussed somewhat later.

The most typical complexes of the porphyrins are those with divalent metals. Certain porphyrins can give unstable, easily hydrolyzed compounds with the univalent alkali metals, in which two metal atoms are apparently bound by ionic bonds to the negatively-charged ring. The porphyrins can also form compounds with the trivalent metals, in which a chlorine atom or other acid radical combines with the system, owing to the third valence of the metal.

The univalent alkali metals, in combining with the porphin ring, give absorption spectra resembling those of the porphyrins in acid media, both in the band positions and in their order of intensity.<sup>[36,75]</sup> This seemingly strange fact can be explained as follows. In acid media, the absorbing species is the doubly-charged porphyrin cation, while in the alkali-metal compounds it is the doubly-charged porphyrin anion, whose  $\pi$ -electron system apparently interacts only weakly with the alkali-metal atoms. The anion and cation of a porphyrin have the same number of  $\pi$ -electrons and the same symmetry properties; hence their absorption spectra are similar. We might say that in both cases we are dealing with the spectrum of the unperturbed porphyrin ring, if we consider complex formation with a metal to be a perturbation of the conjugated system. Indeed, it is rather unclear why the unshared electron pairs on the nitrogen atoms in the porphyrin anion, which should affect the electronegativity of the nitrogen atoms, have practically no influence on the relative positions of the energy levels of the porphin ring.

The data on the absorption spectra of the complexes of porphyrins with divalent metals<sup>[36,46,49,76-78]</sup> can be summarized as follows. The peak wavelength of band I depends (within limits of 30–35  $\text{m}\mu$ ) on the nature of the metal. Here, among the metals of a given group in the periodic table, band I is shifted to longer wavelengths for larger atomic numbers. The position of

band I is related to the stability of the complex.<sup>[77]</sup> The smaller  $\lambda_I$  is, the stabler the complex. The metals of different groups of the periodic table can be arranged in the following order of increasing  $\lambda_I$  (and decreasing stability): Pd < Ni < Co < Cu < Zn < Fe < Mn < Mg < Ba. Williams<sup>[79]</sup> has interpreted this order as being the order of decreasing electron-acceptor properties of the metals,\* and concluded that complex formation reduces the conjugation in the ring. This is because, in many cases of chelate-complex formation in which the metal extends the conjugated system, the absorption band is shifted to longer wavelengths in precisely the opposite sequence. This conclusion has little basis, and can hardly be correct (see below).

The intensity of band I depends rather strongly on the nature of the metal, while that of band II varies little. For mesoporphyrin, the ratio  $J_I/J_{II}$  varies from 3.4 for paladium to 0.65 for cadmium.<sup>[31,47]</sup> For most porphyrins, the intensity of the first band essentially follows the sequence given above in the reverse order: Pd > Ni > Co > Cu > Zn > Mg > Cd. Here the intensity of band I is usually greater than that of band II. In interpreting the spectra theoretically, we must bear in mind that the overall character of the spectrum does not change as the nature of the metal in the center of the molecule changes. In forming a metalloporphyrin molecule, the metal atom is incorporated in a ready-made cyclic structure. For the optical  $\pi$ -electrons, even a strong interaction of the metal with the ring amounts to a relatively minor perturbation of the electronic states. In a first-order approximation, we can assume that the interaction of the  $\pi$ -electrons with the metal results only in a "mixing" of the wave functions of the two electronic excited states involved in the transitions manifested in the absorption spectrum (band I and the Soret band). The greater the "admixture" of the second excited state (the Soret band), the greater is the intensity of band I. Since this effect of "configurational interaction" increases with increasing metal-ring interaction, we can then understand the above-mentioned increase in the intensity of band I accompanying the blue shift in the latter.

We shall discuss from this viewpoint the reason for the intensity anomaly in the metalloporphyrins substituted on the methine bridges. A specially-conducted systematic comparison of the absorption spectra of the metal derivatives of mesoporphyrin and tetraphenylporphin has shown that the effect of the nature of the metal on the positions of the energy levels is the same in both cases, and the anomaly of the metalloporphyrins

\*The tabulated values of the ionization potential, as are ordinarily used to predict the electron-acceptor properties of a metal, do not follow this order strictly. However, we must bear in mind that the tabulated values refer to free metal atoms, and do not reflect the electron-acceptor properties of a metal in which the electron shells have been rearranged by complex formation.

substituted in the  $\alpha$ - $\delta$  positions is observed only in the behavior of the intensity of band I.<sup>[58]</sup> In particular, the greater the intensity of band I in the complex of a given metal with mesoporphyrin, the less it is in the complex of the same metal with tetraphenylporphyrin (for Ni-tetraphenylporphyrin,  $J_I = 0$ ). The behavior of mesoporphyrin is typical of porphyrins substituted on the pyrrole rings, while the above-mentioned similarity between the copper complexes of tetraphenylporphyrin and tetramethylporphyrin permits us to assume that tetraphenylporphyrin is a typical representative of the porphyrins substituted on the methine bridges.

From the standpoint of configurational interaction, this anomaly can be explained by the opposite influences of side-chain substituents in positions 1-8 and positions  $\alpha$ - $\delta$  on the optical-electron states.<sup>[58]</sup> In the molecules of substituted metalloporphyrins, we must take into account two perturbing effects: the effect of the metal atom and the effect of the side-chain substituents. For the porphyrins substituted on the pyrrole rings, the two effects obviously add together, as is evidenced by the increase in the intensity of band I upon increase in either the metal-ring interaction or the number of side-chain substituents. Conversely, for the porphyrins substituted on the methine bridges, the two perturbing factors cancel and compensate one another.\* Total compensation takes place in Ni-tetraphenylporphyrin, for which  $J_I = 0$ .

A possible confirmation of the viewpoint expressed here is the spectra of Pd- and Pt-tetraphenylporphyrin, which were measured by Thomas and Martel.<sup>[80]</sup> Since atoms of palladium and platinum interact more strongly with the porphyrin ring than a nickel atom does (as judged from the positions of the spectral bands), we might expect that the effect of the metal would predominate in these complexes, and  $\epsilon_I$  would differ from zero, with  $\epsilon_I^{\text{Pt}} > \epsilon_I^{\text{Pd}}$ . This is in agreement with experiment.

The concept of configurational interaction was first used (in qualitative form) in describing the spectra of the metal derivatives of tetraphenylporphyrin by Dorough et al.,<sup>[46]</sup> who determined experimentally the oscillator strengths from the absorption curves, and showed that in a number of cases an increase in the oscillator strength of the long-wavelength transition is accompanied by a weakening of the Soret band. Gouterman<sup>[81]</sup> has made a detailed theoretical study of the problem, and was able to explain a number of the spectroscopic properties of metalloporphyrins, in particular

the parallelism in the properties of metalloporphyrins having various side-chain substituents. The most important result of the theory is the establishment of a relation between the frequency of the long-wavelength transition and the oscillator strength: the oscillator strength is proportional to the quantity  $[b(E_Q - E_{Q_0})]^2$ ; here  $E_Q$  is the energy of the lower excited state for a given metalloporphyrin;  $E_{Q_0}$  is the same for a hypothetical "reference" metalloporphyrin having the same side-chain substituents, for which the oscillator strength of the long-wavelength transition is zero; and  $b$  is a certain parameter depending on the nature of the metal-ring interaction. According to Gouterman's estimates, if an "inductive effect" is involved, in which the metal affects the potential of the nitrogen atom, and thus changes the orbital energy of the optical electrons,  $b$  must be 3.6. However, in the case of a "conjugation effect," in which the  $p_z$  orbital of the metal atom is incorporated into the  $\pi$ -electron conjugated system,  $b$  must be equal to unity. Comparison with experiment shows that, on a plot of  $f_Q$  against  $E_Q$ , the experimental points satisfactorily fit the curves calculated for  $b = 1$ . This is interpreted as indicating the predominance of the conjugation effect of the  $p_z$  orbital. The empirical relation between the position of the long-wavelength band and the electronegativity of the metal atom led Gouterman to the following picture of the interaction of the metal with the optical electrons of the porphyrin ring. The unfilled  $p_z$  orbital of the metal atom is incorporated in the overall conjugated system; then, an increase in the electronegativity of the metal atom will increase the  $\pi$ -electron density on it and result in a greater shift in the energy levels.<sup>[81]</sup>

On the basis of the qualitative discussion given above on the intensity anomalies in the metal derivatives of tetraphenylporphyrin, we can ascertain the physical meaning of the quantity  $E_{Q_0}$ . For the porphyrins substituted on the methine bridges, the "reference" metalloporphyrin characterized by the quantity  $E_{Q_0}$  is a complex in which the effect of the metal on the intensity of band I is fully compensated by the effect of the side-chain substituents. For porphyrin, insofar as we can judge from the literature data, the quantity  $E_{Q_0}$  refers to the unperturbed porphyrin ring (the porphyrin anion), in line with the quasi-forbidden nature of the long-wavelength electronic transition. For the porphyrins substituted on the pyrrole rings, the quantity  $E_{Q_0}$  does not refer to any actual metalloporphyrin, but is an empirical constant (the "reference" metalloporphyrin does not exist, since even without interaction with a metal, band I has a non-zero intensity, while interaction with a metal leads only to strengthening of band I).

We must state that the hypothesis that the d-electrons can interact strongly with the  $\pi$ -electrons of the ring<sup>[79]</sup> cannot be rejected on the basis of existing data. Rather, conversely, it is confirmed by the anomalous stability of the complexes of porphyrins with co-

\*We might suggest that the same effect results in the phyllo type in the four-banded spectrum of porphyrins having a  $\gamma$ -substituent. Porphyrin is of phyllo type (with bands I and III very weak), while introduction of substituents into positions 1-8 strengthens bands I and III, giving the etio type. The introduction of a substituent in the  $\gamma$ -position has the opposite effect, somewhat compensating the effect of the substituents on the pyrrole rings, thus giving a phyllo-type spectrum.

balt and nickel. Gouterman's analysis only demonstrates the weakness of this interaction for the optical electrons (as compared with the conjugation effect of the  $p_z$  orbital). We might suggest that it is precisely the effect of the d-electrons which leads to the anomalous spectra of some of the iron-porphyrin complexes.

As has been stated, when some of the pyrrole rings are hydrogenated, the introduction of a metal does not change the absorption spectrum so much as it does in the porphyrins proper. The long-wavelength band remains the most intense of all the bands in the visible. However, its intensity varies from metal to metal. It has been shown for tetraphenylchlorin that the intensity of the first band follows the order  $Mg > Zn > Cd > \text{free base} > Cu > Co$ . Here the sum of the oscillator strengths of the bands in the visible and the Soret band for a given metallochlorin has about the same value as it has for the complex of this metal with tetraphenylporphin.<sup>[47]</sup> In other words, the intensity of the red band arises, so to speak, at the expense of the Soret band. As in the case of the metalloporphyrins, an increase in the metal-ring interaction in a metallochlorin molecule is accompanied by a blue shift of band I.<sup>[47,82]</sup> This indicates the similarity of the wave functions of the excited states in both cases. The metallochlorins show the peculiarity that the intensity of the absorption band in the yellow-green decreases with decreasing wavelength. The metallochlorins differ essentially thereby from the free chlorins, whose spectra in the yellow-green region retain the porphyrin structure.

A characteristic of the absorption spectra of the metal derivatives of the azaporphyrins and phthalocyanines is the presence of an intense long-wavelength absorption band, whose intensity and position depend only slightly on the nature of the metal. The position of this band follows the same order cited above for the porphyrins. Interestingly, the spectrum of Mg-phthalocyanine resembles in form that of chlorophyll, so that Mg-phthalocyanine can be considered to be a synthetic analog of chlorophyll. A parallel study of chlorophyll and Mg-phthalocyanine permitted A. N. Terenin and his school to obtain valuable information on the nature of the primary photochemical reactions of chlorophyll, as is essential in the problem of photosynthesis (see, e.g.,<sup>[83]</sup>).

f) Transitions involving metastable states. Calvin and Dorough were apparently the first to observe the phosphorescence of solutions of metalloporphyrins at low temperatures.<sup>[45]</sup> Their data indicate that the presence of a metal is necessary for phosphorescence. That is, the metal facilitates the transition of the molecule to the metastable triplet state. Subsequent studies have confirmed the phosphorescence of the metal derivatives of various pyrrole pigments. Here it turned out that the quantum yield of phosphorescence for the copper complexes is rather large (from a qualitative estimate). These phenomena have been interpreted

from the viewpoint of the accepted theories of spin-orbital interaction. According to this viewpoint, the introduction into an organic molecule of a heavy or paramagnetic atom (e.g., the copper ion has one unpaired electron and a large nuclear mass) results in "mixing" of the wave functions of the singlet and triplet states. Hence, it increases the probabilities of singlet-triplet transitions, i.e., removes the rule forbidding intercombination.<sup>[84]</sup> This effect should lead to a weakening of the fluorescence, accompanied by a strengthening of the phosphorescence. The lifetime of the latter should decrease as the perturbing effect of the metal increases. Experimentally, one observes a more complex dependence of the fluorescence and phosphorescence on the nature of the metal. This problem will be discussed in further detail in Sec. 5.

Figure 13 shows the phosphorescence spectra of Zn-mesoporphyrin and Zn-tetraphenylporphin at  $-183^\circ\text{C}$ . The frequency spacings observed here are identical with those in the fluorescence spectra at the same temperature. Here, Zn-tetraphenylporphin does not exhibit band splitting (as is also the case in the fluorescence spectrum). This is not remarkable, since the emission in both types of spectra reflects the vibrations of the molecule in the ground state. We might conclude that the symmetry of the electronic orbital wave function of the triplet state is the same as for the singlet state. A peculiarity of the phosphorescence spectra is the appreciably greater intensity of the first band.

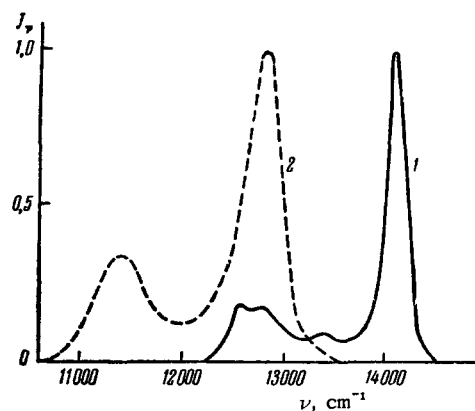


FIG. 13. Phosphorescence spectra at  $T = 77^\circ\text{K}$ : 1 – Zn-mesoporphyrin; 2 – Zn-tetraphenylporphin.

Recently, owing to the studies of Norrish and Porter,<sup>[85,86]</sup> a new approach has been successfully developed in the study of triplet states of molecules. The idea of the method consists in raising an appreciable fraction of the absorbing molecules to the metastable state, using a powerful flash of light of brief duration, and taking the absorption spectrum during an interval of time shorter than the lifetime of the molecule in the metastable state. This new, very promising method of studying biradicals makes it possible to obtain an

amount of new data which could not be obtained by studying the phosphorescence. The application of flash-spectroscopic methods to the study of the porphyrins has begun very recently. A number of studies have been concerned with the bleaching of de-aerated solutions of chlorophyll. [87,88] It was found that alcoholic solutions of chlorophyll are somewhat bleached in the spectral range 465–480 m $\mu$ . On the other hand, the absorption increases in the region of 525 m $\mu$ . The long-wavelength absorption band does not change appreciably, according to the data of [87,88]. The approximate lifetime of the products formed is about  $5 \times 10^{-4}$  sec. Somewhat later, Livingston [89] showed that there are no bands in the red region in the triplet-triplet absorption spectrum, but the band corresponding to the Soret band is split into two strongly-overlapping bands. Subsequent studies by other authors dealing with different porphyrins also indicate a splitting of the band corresponding to the Soret band. [90] A typical absorption curve for one of the porphyrins (tetraphenylporphin) is given in Fig. 14. In this case, there is a weak absorption band in the long-wavelength region of the spectrum. Interestingly, the other compounds, in particular bacteriochlorophyll and the chlorophylls, [91] show no absorption in this region of the spectrum. The described changes in the spectra under the action of powerful brief flashes are currently ascribed to processes involving triplet-triplet absorption. At the same time, the spectral changes under these conditions are strongly reminiscent of the ordinary photochemical processes occurring in solutions under the action of light. [92,93] Thus, great care and caution are required in conducting experiments of this sort and interpreting the results.

A study by Pekkarinen and Linschitz [91] on the metal derivatives of tetraphenylporphin, and also one by Terenin and his associates [94,95] on the metal de-

rivatives of phthalocyanine have demonstrated a close relation between the spectral changes elicited by powerful light flashes and the nature of the central metal atom in the molecules of the compounds being studied. While the insertion of magnesium or zinc atoms into the center of the molecule facilitates the appearance of triplet-triplet absorption, the insertion of copper, nickel, or cobalt leads to a disappearance of the bleaching effect in solution. In this case there is a definite correlation between the ability of the molecules to bleach and the lifetime of the molecules in the metastable state. Hence, the negative result in the study of triplet-triplet absorption of the copper, nickel, and other metal derivatives of the porphyrins is generally explained at present as due to rapid deactivation of the triplet state. If this is true, a shortening of the duration and increase of intensity of the photolytic flash should make possible the observation of triplet-triplet absorption in these cases as well.

In concluding the presentation of the fundamental results of the study of triplet states of porphyrin molecules, we must emphasize again the desirability of careful delimitation of processes of photochemical transformation of molecules under the action of light from processes involving transitions between the triplet states of the molecules. Application of flash-spectroscopic methods also seems very promising in studying photochemical reactions involving molecules of the porphin series, especially for detecting and studying short-lived products of photochemical transformations. The fruitfulness of application of flash methods has been convincingly demonstrated in a recent paper by Terenin and his associates. [96] They observed the appearance of the photoreduced forms of certain chlorophyll-like compounds, which could be ascribed to reversible electron transfer between the molecules of the solvent and the accumulated triplet-state pigment molecules.

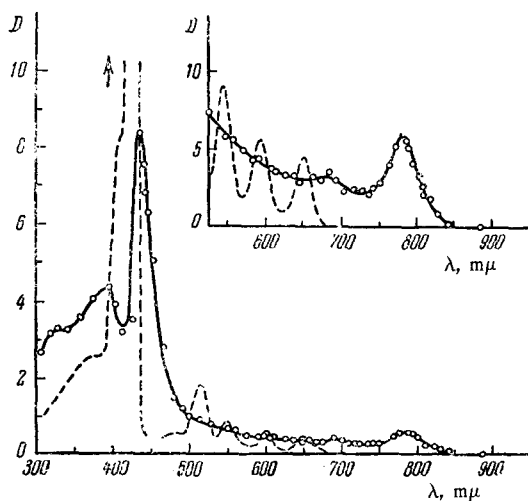


FIG. 14. Triplet-triplet absorption spectrum of tetraphenylporphin. [91]

## 5. QUANTUM YIELD AND LIFETIME OF LUMINESCENCE

An important physical characteristic of luminescent systems is the quantum yield of luminescence, which permits us to draw conclusions on the fate of the absorbed light energy. The value of the lifetime of the luminescence is no less important. A parallel study of the quantum yield and the lifetime permits us to determine the probabilities of radiative and radiationless transitions in the luminescent centers.

Especially attention has been paid to the value of the quantum yield of fluorescence of chlorophyll in connection with the problem of energy transformation in photosynthesis. The first estimate of Prins [97] gave a value of the yield for chlorophyll of 10%. Then Forster and Livingston made measurements using an integrating sphere for a number of pyrrole pigments, and gave for chlorophyll a value  $B = 25\%$ . [98] It

Table I

Substance	B	$\tau \cdot 10^9$ (sec)	$f_{\text{fluor}} \cdot 10^{-6}$ (sec <sup>-1</sup> )	$f_{\text{abs}} \cdot 10^{-6}$ (sec <sup>-1</sup> )
Mesoporphyrin	0.10	13.7	7.3	8.0
Zn-mesoporphyrin	0.07	2.7	27.0	27.0
Protoporphyrin	0.11	12.8	8.6	7.1
Protoporphyrin cation	0.05	2.6	19.0	20.0
Tetrazaporphin	0.12	3.7	32.0	32.0
Mg-tetrazaporphin	0.45	6.2	73.0	83.0
Mg-phthalocyanine	0.80	7.6	108.0	109.0

was later found that this result is also somewhat low, and the value of the quantum yield for chlorophyll a amounts to about 33% (averaged over various solvents<sup>[99-101]</sup>). For the porphyrins, the literature data indicate values of the quantum yield of fluorescence of about 10%.<sup>[88]</sup>

The lifetime of the fluorescence of chlorophyll and its related compounds was measured almost simultaneously by a number of authors.<sup>[102-104]</sup> The value of  $\tau$  for chlorophyll a is  $5.0 \times 10^{-9}$  sec, for pheophytin a it is  $5.5 \times 10^{-9}$  sec, and replacement of magnesium by zinc gives  $\tau = 3.7 \times 10^{-9}$  sec. In<sup>[103]</sup>, the "natural" lifetime of the excited state was also determined from the integrated absorption for the visible bands of chlorophyll; this quantity turned out to agree with the value of  $\tau/B$ .

However, a more systematic comparison of the values of the yield and lifetime of fluorescence, on the one hand, and the integrated absorption, on the other, shows that the relation between these quantities predicted by theory (Kravets' relation<sup>[105]</sup>) holds for the porphyrins, metalloporphyrins, and related compounds, provided that one integrates over the two absorption bands showing mirror symmetry with the emission bands.<sup>[58]</sup>

Table I gives the measured values of the yield and lifetime and the value of the radiative-transition probability  $f$  ( $f = 1/\tau_e$ ), as determined by the two methods (from the integrated absorption and from the luminescence characteristics).

If one integrates the absorption over only the absorption band at the longest wavelengths, or conversely, over all four bands (for a four-banded spectrum), the value of  $f$  determined by the different methods will differ markedly. For example, for protoporphyrin integration over the single band gives  $f = 2.3 \times 10^6 \text{ sec}^{-1}$ , and integration over all four bands gives  $f = 2.6 \times 10^7 \text{ sec}^{-1}$ , whereas  $B/\tau = 8.6 \times 10^6 \text{ sec}^{-1}$ .<sup>\*</sup> Obviously, the conformance to the mirror-symmetry rule in the derivatives of porphin is not due to chance reasons, but reflects the equality of the transition moments for

electronic-vibrational transitions involving the same vibrations in the ground and excited electronic states.

We shall proceed now to the problem of the probabilities of radiationless transitions in the porphin ring. Analogously to the probability of radiative transition, the probability of radiationless transition can be determined from the measured values of the quantum yield and the lifetime of fluorescence:  $d = (1 - B)/\tau$ .

For the metal-free porphyrins, the probability of radiationless transition is ten times that of radiative transition, and amounts to about  $7 \times 10^7 \text{ sec}^{-1}$ . The introduction of light metals (e.g., magnesium) has practically no effect on this value.<sup>\*</sup>

A comparison of the properties of various magnesium complexes shows that aza- and benzo-substitution decreases the probability of radiationless transitions in the porphin ring (for Mg-tetrazaporphin,  $d = 4.5 \times 10^7 \text{ sec}^{-1}$ , and for Mg-phthalocyanine,  $d = 1.3 \times 10^7 \text{ sec}^{-1}$ ). Interestingly, the converse effect is observed in the absence of a metal: aza-substitution increases the value of  $d$ . The chlorophyll molecule shows a probability of radiationless transition twice as great as in the molecules of porphyrins and Mg-porphyrins.

Replacement of the magnesium atom by a zinc atom, which has a greater nuclear charge  $Z$ , appreciably increases the probability of radiationless transition (for Zn-mesoporphyrin,  $d = 1.7 \times 10^8 \text{ sec}^{-1}$ ). At low temperatures the zinc complexes phosphoresce, indicating the existence of another pathway of deactivation of the excited state besides direct conversion to the ground state, i.e., nonradiative transition to the metastable triplet state. The reason for the violation of the rule forbidding intercombination is spin-orbital interaction, which increases proportionally to  $Z^4$ . As has been stated, the phosphorescence of the metalloporphyrins was discovered by Calvin and Dorough;<sup>[45]</sup> the role of spin-orbit interaction was emphasized by Becker and Kasha<sup>[84]</sup> and discussed in detail by Allison and Becker.<sup>[64]</sup> The phosphorescence is especially intense in the Cu-porphyrins, which do not fluoresce. The increase in the probabilities of intercombination transitions, as compared with zinc, may involve the

<sup>\*</sup>We must note that the agreement of the values of  $\tau_e$  obtained by the different methods for chlorophyll by integration over all the visible absorption bands<sup>[103]</sup> can be explained easily by the weakness of the absorption bands of chlorophyll in the yellow-green region of the spectrum.

<sup>\*</sup>For the metalloporphyrins, the calculated results have been reduced by a factor of two, since the excited state is doubly degenerate, as will be shown in Sec. 7.



paramagnetic moment of the copper ion arising from the unpaired electron.

It has been known for a long time that many metalloporphyrins cannot fluoresce. By analogy with the copper complexes, we might suggest that the reason for the lack of fluorescence is the transition of the excited molecules to the triplet state. However, experiment shows that the phosphorescence yield of most of the non-fluorescent metalloporphyrins is considerably less than for the copper complexes, while the lifetime of phosphorescence is not less.<sup>[64]</sup> Thus, the mechanism of spin-orbital interaction does not explain the lack of fluorescence in the complexes of porphyrins with heavy metals, although it apparently plays an essential role in all the complexes.

The nickel and silver complexes of mesoporphyrin practically show neither phosphorescence nor fluorescence. To explain these facts, Gouterman<sup>[106]</sup> suggested that the nickel atom has a low-lying triplet state interacting with the  $\pi$ -electron states of the ring, while the silver atom can act as an electron acceptor after excitation. Both explanations are hypothetical.

An analysis of the experimental data on phosphorescence of metalloporphyrins leads to the following general conclusion. The introduction of heavy metals into porphyrins increases not only the probability of transition to the triplet state, but also the probability of direct conversion to the ground state. Here the relation between these probabilities is determined by the individual characteristics of the electron shells of the metal in the complex, as well as by the characteristics of the side-chain substituents on the porphyrin ring. The latter factor can be highly essential. Thus, in the metal derivatives of tetraphenylporphyrin the phosphorescence is weaker than for the porphyrins substituted in the pyrrole rings.<sup>[58]</sup>

One of the processes of deactivation of the excited state which can occur in the porphyrin ring is the transfer of excitation energy from the ring to the central metal atom. This possibility is indicated by the results of a study of the spectral-luminescence characteristics of rare-earth complexes of phthalocyanine.<sup>[107]</sup> It turned out that the europium complex fluoresces relatively strongly (with a yield of about 15%). The gadolinium complex, which has a very large magnetic moment, fluoresces more weakly, while the ytterbium complex practically does not fluoresce. The ions of europium and ytterbium are similar in properties, but differ in the arrangement of the excited levels: in europium (and also gadolinium), the excited level lies above the singlet level of the phthalocyanine ring, and energy transfer from the ring to the rare-earth ion is impossible. However, energy transfer is possible for ytterbium (the level for ytterbium lies below the level of the ring). Apparently, the lack of fluorescence of the ytterbium-phthalocyanine complex is due to transfer of the excitation energy to the ytterbium ion, with subsequent radiationless deactivation. These

data can be considered as an indirect proof of the possibility of intramolecular energy migration in the porphyrin ring.

In concluding this subsection, we shall discuss the problem of the "activation" of the fluorescence of chlorophyll, which was found almost simultaneously by Evstigneev, Gavrilova, and Krasnovskii,<sup>[108]</sup> and by Livingston, Watson, and McArdle.<sup>[109]</sup> This phenomenon consists in the fact that chlorophyll, which shows a rather high quantum yield of fluorescence in polar solvents (30–35%), does not fluoresce in carefully purified non-polar solvents. Upon addition of very small amounts of polar substances (water, alcohols, amines, etc.), the yield rapidly increases, attaining the values cited above. Mg-phthalocyanine behaves analogously; however, other metalloporphyrins and metallochlorins do not show the phenomena, nor does free pheophytin.

Thus far there has been no reliable explanation of the phenomenon of activation of fluorescence. There are two diametrically-opposed viewpoints. According to one of these, advanced by Evstigneev,<sup>[110]</sup> non-fluorescent dimers are formed in pure non-polar solvents. Then the activation of fluorescence is explained by disaggregation by the action of the polar molecules. According to the other viewpoint, the free chlorophyll molecule cannot fluoresce, but becomes fluorescent only upon combining with a polar molecule.<sup>[109,111,112]</sup> Certain authors<sup>[111,112]</sup> explain the hypothetical non-fluorescence of unbound chlorophyll molecules by suggesting that the chlorophyll molecule can undergo  $n \rightarrow \pi^*$ -transitions, the frequency of the  $n \rightarrow \pi^*$ -transition being lower than that of the long-wavelength  $\pi \rightarrow \pi^*$ -transition. If this is true, the probability of radiative transition from the lowest excited state to the ground state will be small, and this transition will occur by the radiationless pathway. However, if a polar substance is bound to the molecule, the frequency of the  $\pi \rightarrow \pi^*$ -transition will become smaller than that of the  $n \rightarrow \pi^*$ -transition, and the probability of radiative transition from the lowest excited state to the ground state will thus increase markedly, which would explain the activation of fluorescence. The phosphorescence of chlorophyll found by Fernandez and Becker<sup>[113]</sup> in pure non-polar media at liquid-nitrogen temperature (there was practically no fluorescence at room temperature) was ascribed to a transition from the triplet state  $^3(n, \pi^*)$  to the ground state, and viewed as a confirmation of the given hypothesis.

There is apparently no basis for the idea that unbound chlorophyll molecules cannot fluoresce. First, all other fluorescent metalloporphyrins, including Zn-pheophytin, fluoresce even in dry non-polar solvents. Second, all known chelates of magnesium are capable of fluorescing. Third, the appearance of  $n \rightarrow \pi^*$ -transitions in the region of the long-wavelength absorption band of chlorophyll is improbable from general

considerations, and is not in accord with the short lifetime of the above-mentioned phosphorescence. The problem of the activation of fluorescence of chlorophyll may be directly related to that of the mechanism of the primary photosynthetic reactions. Further study along this line is obviously necessary.

## 6. POLARIZED FLUORESCENCE OF PORPHIN DERIVATIVES

a) Limiting polarization of the luminescence and symmetry of the structures of porphyrin molecules. The study of polarized fluorescence is one of the very effective methods of molecular spectroscopy. The study of the anisotropy of the processes of absorption and emission of light in molecules provides valuable information on the properties of the molecular oscillators, and in a number of cases also on the structure of molecules.<sup>[59,114]</sup> However, we must note that systematic studies of the polarization of the fluorescence of porphyrins have essentially just begun in recent years, in spite of their obvious necessity in understanding the nature of the optical processes in the porphin ring.

The anisotropy of emission (polarization of fluorescence) of isotropic solutions manifests the anisotropy of the elementary molecular oscillators and the anisotropy of the exciting light. Upon excitation with plane-polarized light having the electric vector vertical, those molecular oscillators are preferentially excited which have orientations near the vertical. If the emitting oscillators coincide in direction with the absorbing oscillators, and the molecules are rigidly fixed in the medium, then the vertically-oriented oscillators will preferentially emit. Hence, the luminescent light propagated in the horizontal direction will be partially polarized. The degree of polarization is defined as  $(J_z - J_x)/(J_z + J_x)$ , where  $J_z$  and  $J_x$  are the intensities of vibration of the electric vector in the vertical and horizontal directions. As is shown by calculation, this quantity must be one-half when the linear oscillators for absorption and emission coincide in direction. These directions coincide for the oscillator of the long-wavelength absorption band and the luminescence oscillator (the vibrations of the nuclei forming the molecular skeleton ordinarily interfere somewhat with this coincidence). Below, we shall designate as the limiting polarization the quantity  $P_0$ , as measured in this particular special case, i.e., with excitation in the long-wavelength absorption band, as close as possible to the frequency of the 0-0 transition.

We can apply the linear-oscillator model only to molecules of sufficiently low symmetry. In planar molecules having symmetry axes of order higher than twofold, severally equally-probable directions are possible for an oscillator lying in the plane of the molecule. Then we must take a so-called "planar oscillator" as the model for the processes of light absorption and emission. The components of this oscillator in any

mutually-perpendicular directions  $x$  and  $y$  in the plane of the molecule are identical, but the component along the  $z$  axis is zero. From the quantum-mechanical viewpoint, this involves the existence of doubly-degenerate states in molecules of high-symmetry. The theoretical value of the limiting polarization for a set of planar oscillators is one-seventh.<sup>[115]</sup> Thus there is a relation between the symmetry of the molecules and the limiting polarization of luminescence. This makes it possible to study experimentally the symmetry of molecules by the polarization method.

The limiting-polarization method has been applied to study the molecules of porphyrins.<sup>[67,68]</sup> Until recently, there were no x-ray diffraction data on the symmetry of molecules of porphyrins (it was only shown that the molecules of porphyrins are planar<sup>[116]</sup>). Robertson and his associates have made a complete x-ray diffraction analysis of the phthalocyanines.<sup>[13,117,118]</sup> While these studies are considered classic, their results do not permit us to draw definite conclusions on the symmetry of the metallophthalocyanine molecules, not to speak of the porphyrins. According to Robertson, the metal-free phthalocyanine molecule is elongated in form, while the insertion of a nickel atom reduces the deviation from tetragonal symmetry, but not completely (to 0.06 Å, as compared with 0.12 Å). An x-ray diffraction analysis recently performed by Crute<sup>[119]</sup> on Ni-etiochlorophyll also does not permit us to decide on the "fine structure" of the center of the porphin ring. We must note that the limiting-polarization method of studying symmetry has the advantage that it permits us to obtain simultaneously information on the properties of the long-wavelength oscillator, as is necessary in interpreting the spectrum. The experimental values of the limiting polarization of fluorescence determined by extrapolation to infinite viscosity for Mg-tetraphenylporphin, Zn-tetraphenylporphin, Mg-tetrazaporphin, and Mg-phthalocyanine (12-13%) were lower than the theoretical value of one-seventh (Fig. 15). If we take into account the structural formulas of these compounds and the planar structure of the conjugated systems, we can then conclude that the molecules of the symmetrically-substituted metalloporphyrins, and hence also of the metal derivatives of unsubstituted porphin, belong to point group symmetry  $D_{4h}$ . Such a high symmetry implies complete equivalence of the symmetrically-related atoms and bonds, the equivalence of the pyrrole rings, and the basence therein of "semi-isolated" double bonds. In particular, all four Mg-N bonds are completely equivalent. In essence, symmetrical aza- and benzo-substitution does not destroy the  $D_{4h}$  symmetry of the molecule.\*

Undoubtedly, the high symmetry of the studied

\*We make this statement, which seems trivial, since recently Mason,<sup>[14]</sup> in analyzing the cited studies of Robertson, came to the incorrect conclusion of the existence of "conjugation distortion" in the phthalocyanine ring in the presence of a metal.

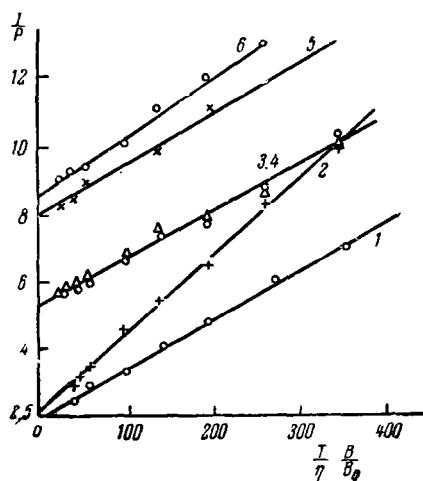


FIG. 15. The relation of  $1/P$  to  $(T/\eta) \cdot (B/B_0)$  for: 1—chlorophyll a; 2—tetraphenylporphin; 3—Zn-mesoporphyrin; 4—mesoporphyrin in acid medium; 5—Zn-tetraphenylporphin; 6—Mg-phthalocyanine.

molecules is due to the effect of conjugation (delocalization of the  $\pi$ -electrons). In distinction from the well-studied case of benzene, the effect of conjugation in the porphin ring does not lead to complete equivalence of all bonds, since the geometry of the tetrapyrrole conjugated ring does not permit symmetry higher than fourfold.

High values have been obtained for the limiting polarization of the metal-free porphyrins, close to one-half, and hardly differing from the known values of the limiting polarization of luminescent dyes. These facts indicate that the neutral molecules of porphyrins do not have symmetry axes of order higher than twofold. We can also conclude that the hydrogen atoms in the center of the porphyrin molecule occupy fixed sites, and do not migrate freely from one nitrogen atom to another, since in the latter case the emitting oscillator would change in orientation and the luminescence would be strongly depolarized. Since the emission process has a lifetime of the order of  $10^{-8}$  sec, the period during which the central protons remain in fixed sites must be longer than this value.\*

The assignment of the neutral porphin molecule to a particular twofold symmetry group involves the determination of the positions of the central hydrogen atoms. In addition to the natural assumption that the protons are located on opposite nitrogen atoms, there are also other hypothetical possibilities. However, as was noted above (Sec. 3), these hypotheses are contradicted by a number of experimental facts, in particular the data of infrared spectroscopy.

\*Erdman and Corwin arrived at this conclusion as early as 1946.<sup>[75]</sup> However, their arguments, based on the similarity of the absorption spectra of etioporphyrin and N-methyletioporphyrin, have been criticized.<sup>[51]</sup> The results of the polarization measurements essentially confirm this conclusion.

Thus we arrive at the following picture of the structure of the neutral porphin molecule and its symmetrically-substituted derivatives. These molecules belong to the point group  $D_{2h}$ , with the hydrogen atoms in the center of the molecule attached to opposite nitrogen atoms by ordinary covalent bonds. The imine nitrogen atoms joined to the hydrogen atoms are not equivalent to the tertiary nitrogen atoms, which bear unshared electron pairs. Consequently, the equivalence of the pyrrole rings is destroyed, resulting in symmetry  $D_{2h}$ .

In the case of mesoporphyrin and protoporphyrin, which contain asymmetrically-arranged side-chain substituents, the limiting polarization of the metal derivatives and cations formed in acid media is also very small (17–18%), although it is greater than one-seventh. These results permit us to assign an approximate symmetry  $D_{4h}$  to the conjugated systems of the asymmetrically-substituted metalloporphyrins and the corresponding cations. Thus, a process takes place on introduction of two extra protons into the center of the porphyrin molecule analogous to that which occurs when a metal is introduced. The four nitrogen atoms become equivalent, and the electron-cloud density is equalized. We must note that the upward deviation from one-seventh in these cases is outside the experimental errors. Hence, the symmetry is only approximately fourfold. On the other hand, these data indicate the high sensitivity of the limiting-polarization method, since alkyl-type side-chain substituents do not enter into conjugation with the ring. That is, they interact weakly with the optical  $\pi$ -electrons; this, in particular, is manifested in the small effect of these substituents on the electronic spectra.

For the most important pyrrole pigment, chlorophyll, the limiting polarization is high, and does not differ from that of pheophytin (42%), in spite of the presence of the magnesium atom in the center of the molecule. This can be easily explained by the fact that the symmetry of the conjugated system is markedly reduced by the hydrogenation of one of the pyrrole rings, and the introduction of the metal does not increase the symmetry of the molecule. The chlorin molecule has only a single twofold axis (symmetry  $C_{2v}$ ), and a metallochlorin molecule has the same symmetry. By analogy with the metalloporphyrins, we can assume that the three nonhydrogenated pyrrole rings of the metallochlorin are equivalent, so that hydrogenation of one of the four equivalent pyrrole rings does not destroy the equivalence of the other three. Correspondingly, the structures of metallochlorins do not contain "semi-isolated" double bonds. Just as in the metalloporphyrin molecules, the bonds of the metal atom to three of the nitrogen atoms should be identical (the question is somewhat unclear as to whether the bond of the metal to the nitrogen of the hydrogenated pyrrole ring can be equivalent).

b) Polarization spectra and an oscillator model of porphyrin molecules. The results presented above

from the study of polarized luminescence of porphyrins refer to the case of excitation in the long-wavelength absorption band (with absorption and emission oscillators coinciding in direction).

If we go to excitation in the other absorption bands, the degree of polarization of the luminescence changes sharply, often taking on negative values. The characteristic dependence of the degree of polarization on the wavelength of excitation is called the polarization spectrum. Analysis of polarization spectra permits us to determine the approximate mutual orientation of the molecular oscillators corresponding to the different absorption bands (since the luminescence oscillator coincides in direction with the long-wavelength absorption oscillator). The polarization spectrum, combined with the value of the limiting polarization, is a very important characteristic of polarized luminescence, and is of fundamental significance in analyzing molecule spectra. [59,114]

We shall discuss now the polarization spectra of the porphyrins. In all the cases of low limiting polarization mentioned above, the degree of polarization was independent of the wavelength of the exciting light; this is an additional confirmation of the high symmetry of the molecules and the existence of a planar emission oscillator.\*

The polarization spectrum of a metal-free porphyrin (tetraphenylporphyrin) was first measured by Weigl [56] with the aim of checking the theoretical study of Platt. [111] Weigl was not aware of the dependence of the degree of polarization on  $\lambda_{\text{emission}}$ , and made the measurements of the degree of polarization essentially in the first emission band; the light to be analyzed contains an appreciable proportion of the second emission band only when the excitation is in band I. Thus he obtained a low value for the degree of polarization (28%) for viscosities approaching infinity.

As the experimental studies have shown, the degree of polarization of the fluorescence of porphyrins depends markedly on the wavelength of emission. Here,

\*It is pertinent to mention here that analogous phenomena (a low degree of polarization of fluorescence, independent of the wavelength of excitation) were found considerably later in a study by Bär, Lang, Schnabel, and Kuhn, [120] who also ascribed them to high symmetry of the molecules. However, the German authors did not determine the value of the limiting polarization. Besides, reference [120] contains a number of false assumptions which we shall take up in the next section, which is concerned with the interpretation of the electronic spectra. In the paper of Bär et al., one is somewhat puzzled by the absence of references to the work of P. P. Feofilov, [115] who established the relation between the limiting polarization and the molecular symmetry. These authors obtain anew the theoretical value of one-seventh, but incorrectly, the calculation being based on the physically incorrect idea of two types of molecules, in which the angles between the oscillators for emission and for long-wavelength absorption are  $0^\circ$  and  $90^\circ$ , respectively. There is also no reference to a study published two years earlier, [67] in which the polarization method was first used to study the symmetry of porphyrin molecules.

the second emission band shows a low positive value for the degree of polarization when excited in the long-wavelength absorption band. [121] In order to find the basis of the difference between the two fluorescence bands, and to study the orientation of the molecular absorption oscillators, studies were undertaken of the polarization spectra of the porphyrins for each of the emission bands individually. [122]

The measurements showed that the polarization spectra of different porphyrins measured for the first fluorescence band were similar. When the excitation is in absorption band I,  $P$  has a high positive value, but in band III it is negative, while bands II and IV give small positive values of  $P$  (Fig. 16). An important peculiarity of the polarization relations in the porphyrins is the mirror symmetry about the frequency of the 0-0 transition in the portion of the polarization spectrum spanning absorption bands I and II and in the curve of  $P$  against  $\lambda_{\text{emission}}$ .

The measurements in the second fluorescence band showed a degree of polarization practically independent of the wavelength of excitation (Fig. 16). This form of polarization spectrum is quite natural for highly-symmetric molecules, but such a result is uncommon for molecules of low symmetry, and had not been previously observed.\* The independence of  $P$  from  $\lambda_{\text{excitation}}$ , and the closeness of the values of  $P$  to one-seventh indicate that the emitting oscillator has approximately equal components in two mutually-perpendicular directions in the plane of the molecule; that is, it is a planar oscillator. We could try to fit to the second emission band a model of a linear oscillator rotated by  $45^\circ$  with respect to the oscillator for the first band in the plane of the molecule. However, the symmetry of the system requires the introduction of a second oscillator of the same kind, rotated by  $-45^\circ$  with respect to the oscillator of the first band, and this is equivalent to a planar oscillator.

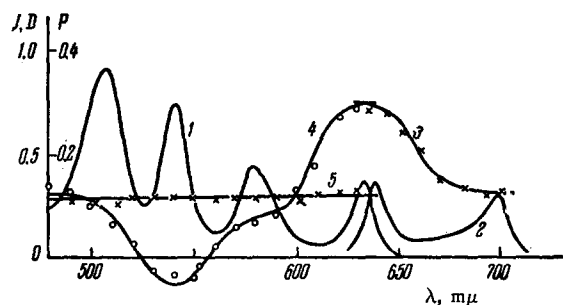


FIG. 16. Polarization spectra of protoporphyrin. 1 - Absorption spectrum; 2 - luminescence spectrum; 3 - relation of  $P$  to  $\lambda_{\text{emission}}$  for excitation in band I; 4 - relation of  $P$  to  $\lambda_{\text{excitation}}$  when measured in band I; 5 - the same, when measured in band II.

\*We must note that the leveling-out effect of the polarization spectrum when one goes to the second emission band was also found in the above-mentioned study of Bär, Lang, Schnabel, and Kuhn. [120]

Thus, the observed difference in the polarization spectra for the two fluorescence bands can be interpreted only in terms of the idea that two oscillators are responsible for the two bands in the emission spectrum. These oscillators differ in their physical properties: the first band corresponds to a linear oscillator, while the second band corresponds to a planar oscillator. On the basis of this result, we can carry through the construction of an oscillator model of the optical processes in the porphyrin molecules.

For symmetry  $D_{4h}$ , all of the absorption and emission bands correspond to planar oscillators. For symmetry  $D_{2h}$ , the first and third absorption bands correspond to linear oscillators, while the second and fourth absorption bands correspond to planar oscillators; in emission, the first band corresponds to a linear oscillator coinciding in direction with the oscillator of the long-wavelength absorption, while the second band corresponds to a planar oscillator. All of the oscillators lie in the plane of the molecule.

Measurements have also been made on the polarization spectra of pheophytin a for the first and second fluorescence bands (Fig. 17). In this case, the degree of polarization depends considerably more weakly on the emission wavelength than in the porphyrins. Correspondingly, the polarization spectra for the two emission bands do not differ much from one another.

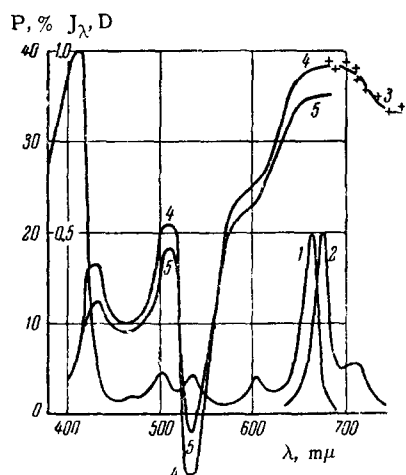


FIG. 17. Polarization spectra of pheophytin. 1—Absorption spectrum; 2—luminescence spectrum; 3—relation of  $P$  to  $\lambda_{\text{emission}}$  for excitation in the long-wavelength absorption band; 4 and 5—polarization spectra as measured in luminescence bands I and II, respectively.

Analogously to the case of pheophytin, the measurements on tetrazaporphin did not show an appreciable dependence of  $P$  on  $\lambda_{\text{emission}}$ . Since both of these compounds have intense long-wavelength absorption bands, we are driven to the conclusion that such a dependence is observed only when the long-wavelength band is weak. In other words, the existence of a planar oscillator in emission apparently involves the quasi-forbidden character of the long-wavelength electronic transition in porphyrin molecules.

In the case of tetrazaporphin, the degree of polarization with excitation in the first absorption band has

a large positive value (limiting polarization 40%). With excitation in the second band, it has a high (in absolute value) negative value ( $-17\%$ ). Thus, the two intense absorption bands of tetrazaporphin, which merge into one upon introduction of a metal, correspond to two mutually-perpendicular linear oscillators. An analogous result was obtained by Bär et al. [120] for sulfonated phthalocyanine.

A study of the polarization spectrum of pheophytin shows that it resembles closely that of protoporphyrin. In particular, band III in the absorption spectrum of pheophytin shows a negative polarization; when we go to band IV, the polarization changes sign. If we take into account the fact that bands III and IV in the spectrum of pheophytin differ little in position and intensity from the corresponding bands of protoporphyrin, we might assume that the hydrogenation of one of the pyrrole rings does not affect the orientation of the oscillator for band III, just as it does not affect its other properties. If this is true, then the oscillator for band I also maintains its orientation, but changes only in oscillator strength and frequency. Thus, the effect of hydrogenation can be reduced to a change ("perturbation") of the electronic levels of the porphyrin ring. This viewpoint has been expressed previously by Platt [111] and Seely [123] on theoretical grounds. However, as yet there are no sufficient grounds for rejection of the hypothesis of Rabinowitch that a new excited level appears upon hydrogenation.

In conclusion, we shall discuss the polarization spectrum of chlorophyll. The great role of chlorophyll in living nature makes it the most interesting object of study, and it is not by chance that the studies of polarized fluorescence of the pyrrole pigments began precisely with chlorophyll. The first measurements were made by F. Perrin, who determined the degree of polarization extrapolated to infinite viscosity for three wavelengths of the exciting light, corresponding to the Soret band and the long-wavelength absorption band. [124] Individual regions of the polarization spectrum of chlorophyll were measured by Feofilov. [125] In 1952, Stupp and Kuhn [126] published a polarization spectrum, which Kuhn subsequently was obliged to retract. [120] Finally, Goedheer [127] measured the polarization spectrum of chlorophyll over a wide range of wavelengths with considerable accuracy, and studied also pheophytin, bacteriochlorophyll, and bacterio-pheophytin. [127] Our data for chlorophyll and pheophytin agree satisfactorily with Goedheer's results, as well as with those of Perrin and Feofilov. Here the study of the metal derivatives of pheophytin showed that the polarization spectrum of chlorophyll is typical of the metallopheophytins. [82]

The polarization spectrum of chlorophyll contains no such region of negative polarization as does that of pheophytin. However, the polarization spectrum shows a minimum (with  $P$  near zero) in the region of band

III. If we take into account the considerable overlap of the bands in the yellow-green region of the spectra of the metallochlorins, we might assume that band III corresponds to an oscillator oriented perpendicularly to that of the long-wavelength band. We can interpret this as a decrease in the frequency of the corresponding oscillator (for band III) of pheophytin. In line with what was said above on the similarity of properties of the excited levels of the porphyrins and the chlorins, this shift in the band is quite natural. In fact, when a metal atom is introduced into the unhydrogenated porphyrin ring, the pyrrole rings become equivalent, and the frequencies of the mutually-perpendicular oscillators of bands I and III, which pass through the pyrrole rings, become equal, giving rise to a planar electronic oscillator. Here the frequency of the oscillator for band III diminishes, while that of band I increases. When there is a hydrogenated pyrrole ring, the symmetry is lowered, and the bands cannot merge, but the general tendency of the band shifts must be the same, which is what one observes experimentally. However, the polarization spectra of the chlorins and metallochlorins cannot yet be considered to have been interpreted in detail, and further studies are obviously necessary.

## 7. THE INTERPRETATION OF THE ELECTRONIC SPECTRA OF PORPHYRIN MOLECULES

### a) The theoretical study of the spectra of porphyrins.

The important role of the porphyrin pigments in the photosynthesis process cannot be completely elucidated without exhaustive information on the lowest excited state of the molecules. Hence, the interpretation of the electronic spectra of the porphyrins has attracted and continues to attract many investigators. The first attempts to interpret the spectra of this class of compounds were made in the thirties. Various authors arrived independently at similar viewpoints, the essence of which amounts to the following: all four absorption bands in the visible belong to one electronic transition, while the Soret band belongs to another.

[32,35,37,63,97] The basis of this hypothesis was the approximate equality of the frequency intervals between the consecutive spectral bands of the porphyrins, and the closeness of these intervals to the vibration frequencies manifested in the electronic spectra of polyenes. This hypothetical interpretation became widespread, and entered into the monograph literature. [3]

Considerably later, Blyumenfel'd [128] advanced a complete opposite interpretation of the spectra of the porphyrins. According to this hypothesis, all the absorption bands correspond to separate electronic transitions. Using the group-theoretical method, Blyumenfel'd explained satisfactorily certain regularities in the spectra of porphyrins. However, this interpretation involves great difficulties. In particular, this hypoth-

esis cannot explain why the fluorescence spectrum contains two bands rather than one, as usually happens with complex molecules.

A number of theoretical studies have appeared recently whose authors have tried to calculate the positions of the energy levels of the porphyrin system. These studies have led to concepts essentially different from the hypotheses described above. The calculations were conducted by various modifications of the molecular-orbital method (the free-electron method and the linear combination of atomic orbitals (LCAO method)). We must note here that these attempts at theoretical treatment of the spectra of porphyrins are based on crude theoretical models, and cannot pretend to solve the problem rigorously. Thus, any experimental facts permitting any progress whatever toward solution of this problem would be of the utmost significance.

The first theoretical study on the spectroscopy of the porphyrins was that of Simpson. [129] He applied the LCAO method with great simplifications (he assumed complete aromaticity of the porphyrin ring, neglected the electronegativity of the nitrogen atoms, etc.), and thus constructed an energy-level diagram of the molecule. However, the long-wavelength electronic transition, according to these calculations, should occur in the infrared. Since this conclusion does not correspond to reality, he concluded that the porphyrin ring is not completely aromatic. Here he had to assume that the two lateral double bonds and the two nitrogen atoms attached to hydrogen atoms are isolated from the conjugated system, and hence, there are two isomers of porphyrin,  $D_{2h}$  and  $C_{2v}$ . A corresponding calculation on a model of free electrons in a closed circuit was calibrated from the benzene spectrum, and gave a value  $\lambda = 615 \text{ m}\mu$  for the "center of gravity" of the bands. The author considered this result satisfactory in view of the crudeness of the initial assumptions.

In Simpson's "free-electron" model, the transitions occur between orbitals  $e^{\pm 4i\varphi}$  and  $e^{\pm 5i\varphi}$ . In the ground state, the system has a total angular momentum of zero ( $+4 + 4 - 4 - 4$ ). When one electron goes over to an  $e^{\pm 5i\varphi}$  orbital, two cases are possible:  $L = \pm 1 \times (+4 + 5 - 4 - 4)$ , or  $(+4 + 4 - 4 - 5)$ , and  $L = \pm 9 \times (+4 + 4 - 4 + 5)$ , or  $(+4 - 5 - 4 - 4)$ . Thus, degenerate states arise, of which the state with  $L = \pm 9$  is lower, in agreement with Hund's multiplicity rule. The transitions with  $\Delta L = \pm 1$  are allowed, while those with  $\Delta L = \pm 9$  are forbidden. Thus the weakness of the long-wavelength absorption bands of the porphyrins is explained. The four-banded spectrum results from the superposition of the spectra of the two isomers and the removal of the degeneracy owing to the low symmetry of the molecules of the isomers. The Soret band corresponds to the four allowed transitions, which differ little spectroscopically. Thus, in contradiction to the "vibrational" hypothesis, all four absorption bands

of porphin are ascribed to distinct electronic transitions, although they involve the existence of tautomeric forms.

Calculations by the LCAO method performed somewhat later, however, took into account the electronegativities of the nitrogen and carbon atoms.<sup>[130]</sup> In predicting the spectra of porphin and tetrahydroporphin, corrections for overlap of atomic orbitals were introduced. The value of the parameter  $\beta$  was assumed to be  $23000 \text{ cm}^{-1}$  by analogy with other cyclic conjugated systems. The symmetry of the molecule was assumed to be  $D_{4h}$  in the calculation. When the electronegativity of the nitrogen atoms is not taken into account, the results agree with those of Simpson: the transition at longest wavelengths turns out to be in the infrared. The authors ascribe this to the defects of the calculation. The calculations predict an  $a_{2u} \rightarrow e_g$  transition corresponding to the long-wavelength absorption band, and two transitions,  $a_{1u} \rightarrow e_g$  and  $b_{2u} \rightarrow e_g$ , corresponding to the Soret band. Thus, two electronic transitions are predicted in the visible, since the degenerate levels split. When the electronegativity of the nitrogen atoms is taken into account, the picture becomes more complicated: two doubly-degenerate transitions are found in the visible, or four if splitting is taken into account.

Essential changes do not arise in the "free-electron" method<sup>[131]</sup> when the branching of the conjugated bond system of porphin and the presence of the heteroatoms are taken into account. Then, two doubly-degenerate transitions are still predicted for porphin in the visible, but the results agree better with experiment. The positions of these absorption bands turn out to be:  $a_{2u} \rightarrow e_g$  transition =  $640 \text{ m}\mu$ ;  $a_{1u} \rightarrow e_g$  transition =  $495 \text{ m}\mu$ .

Matlow<sup>[132]</sup> has tried to take into account the difference between the imine and tertiary nitrogen atoms. However, the calibration of the calculation with a long-wavelength absorption band of porphin with a peak at  $634 \text{ m}\mu$  renders the obtained results useless, since this peak, as was found, belongs to an impurity, rather than porphin itself.<sup>[50]</sup> The author came to the conclusion that porphin is a mixture of two isomers, and dihydroporphin of three.

Recently Kuhn and Huber<sup>[133]</sup> performed some calculations for porphin and tetrahydroporphin by the free-electron method, taking into account the symmetry of the system and the electronegativity of the nitrogen atoms. The ascribing of a determining role to the nitrogen atoms resulted in an exchange of position of the predicted transitions, as compared with those given by the previous authors, but did not give any other new results. A use of the LCAO method taking into account the self-consistent field<sup>[134]</sup> led to the prediction for porphin of one doubly-degenerate transition for symmetry  $D_{4h}$ , and two transitions for lower symmetries. We must note that arbitrarily chosen parameters were used even in this case.

Finally, Platt<sup>[111]</sup> has suggested the following semi-empirical interpretation of the spectra of the porphyrins. Here he relied on the results of the calculations, and used the hypothesis of Erdman and Corwin,<sup>[75]</sup> which the latter had proposed as early as 1946, that the four-banded spectrum corresponds to symmetry  $D_{2h}$ , and the two-banded spectrum to  $D_{4h}$ . Since porphin in acid media has practically a single-banded spectrum, Platt suggested interpreting this band as the 0-1 transition, and assuming that the 0-0 transition is forbidden by the selection rule for the angular momentum (according to Simpson), while the vibrations remove the rule forbidding the transition. The introduction of side-chain substituents destroying the exact  $D_{4h}$  symmetry of the molecule leads to the appearance of a weak absorption band corresponding to the 0-0 transition. He suggested that the doubly-charged porphyrin ions have two doubly-degenerate states, transition to one of them being forbidden, but that to the other state being allowed (the Soret band). Lowering of the symmetry removes the degeneracy, and a four-banded spectrum results. Thus, bands I and III belong to different electronic transitions, while bands II and IV are due to the superimposition of vibrations. The hypothesis advanced by Platt described satisfactorily most of the known experimental facts. However, the polarization measurements of Weigl,<sup>[56]</sup> as has been noted, showed that each absorption band has its own value for the degree of polarization in the polarization spectrum. This confirms a system of four electronic levels, rather than two.

Thus, the theoretical treatment of the problem by crude quantum-chemical methods gives ambiguous results, and at present does not permit a reliable interpretation of the electronic spectra of the porphyrins. Obviously, a careful analysis of the experimental data is needed for the creation of a well-grounded interpretation of the spectra of the porphyrins.

b) Experimental evidence. In arriving at a correct interpretation of the spectra of the porphyrins, the following experimental facts are essential:

1. When a porphyrin molecule binds a metal atom or two extra protons (in acid media), the four-banded spectrum becomes two-banded, while the Soret band is practically unchanged. As has been noted, it has been shown experimentally that this involves a transition from symmetry  $D_{2h}$  to symmetry  $D_{4h}$ , and that the long-wavelength transition in molecules of porphyrins in acid media and metalloporphyrins involves doubly-degenerate states.<sup>[68]</sup> These facts clearly disagree with the first hypothetical interpretation of the spectra of the porphyrins, but can be explained easily by the second and third interpretations.

2. The emission spectra of the porphyrins contain two bands, independently of the number of bands in the absorption spectrum. These emission bands are mirror images of the two absorption bands at longer wavelengths, and do not depend on the wavelength of excita-

tion (see Sec. 4). This fact cannot be explained by the first or second hypothesis, since vibrations manifested in the absorption spectrum must also be manifested in the luminescence spectrum, according to Levshin's rule of mirror symmetry.<sup>[59]</sup> Hence, under the first interpretation, we should expect four bands in the emission spectrum, and one band under the second interpretation. In general, if we assume that porphyrin molecules can have two closely-spaced ground levels, we can explain the mirror symmetry of the spectra on the basis of the second hypothesis as well, on the basis of chance agreement of the energy spacings of the lower and upper levels. However, the mirror-symmetry rule, which is rather well obeyed, imposes here some definite requirements also on the wave functions of these states; this makes such an assumption improbable. Besides, mirror-symmetry is observed also in the polarization properties, which would require even more artificial assumptions. The essential argument in favor of the vibrational origin of band II and the assignment of bands III and IV (for the four-banded spectrum) to another electronic transition is the agreement between the values of the radiative-transition probabilities, as determined from the integrated absorption and from the luminescence characteristics ( $\tau$  and  $B$ , see Sec. 5). We find such an agreement only if we interpret absorption bands I and II as the mirror images of the emission bands. Obviously, the observance of the mirror-symmetry rule in the porphyrins is not due to chance. We must note that the fact that the emission spectra are independent of the wavelength of excitation, as well as the existence of a structured polarization spectrum, renders it impossible to interpret the porphyrin bands as belonging in pairs to two tautomeric forms.

3. The first and third bands in the spectrum of porphyrin have exceedingly low intensities ( $f \sim 0.01$ ), and in acid media band I is very weak.<sup>[40]</sup> The introduction of various side-chain substituents affects the general character of the spectrum only slightly, but the intensities of bands I and III are more sensitive to these influences than bands II and IV.<sup>[7]</sup> The weakness of the absorption bands suggests that the corresponding transitions are quasi-forbidden in nature. This does not contradict the first of the hypotheses under discussion. However, it is very hard to explain the difference in the sensitivities of the different bands to small structural changes and the intensity distribution in the absorption spectrum of porphyrin if we adopt this viewpoint. Under the second hypothesis, the questions remain unexplained why all the absorption bands in the visible spectrum are quasi-forbidden, and why there is such a selective sensitivity to structural changes. On the other hand, the third hypothesis explains these facts naturally. Indeed, if the transition is forbidden, and the absorption bands appear only as a result of the perturbing effect of the vibrations, then the introduction of side-chain substituents destroying

the symmetry of the system will affect the intensity of the forbidden transition, but affect very weakly the bands arising from removal of the selection rule by the vibrations.

4. Since the degree of polarization changes sign twice within the limits of the absorption spectrum in the visible, the first hypothesis hardly agrees with experiment. Some improbable assumptions are needed to reconcile the second hypothesis with these experiments: for example, to explain the existence of a planar oscillator for the second emission band, we must assume that two levels closely spaced in energy are located near the ground state (degenerate states are impossible for symmetry  $D_{2h}$ ). However, the third hypothesis easily explains these facts without artificial assumptions. Taking into account the quasi-forbidden nature of the long-wavelength transition in porphyrin molecules, all that is required here is to consider the essential role of the vibrations as a perturbing factor removing the selection rule, as will be discussed below.

An analysis of the cited set of experimental data permits us to determine the symmetry of the electronic and vibrational states manifested in the spectra of porphyrins.<sup>[135]</sup>

c) An interpretation of the electronic-vibration spectra. As is known, group theory permits us to classify the electronic and vibrational states of molecules according to the transformation properties of the wave functions with respect to various symmetry operations. The  $\pi$ -electrons have the peculiarity that their orbitals are necessarily antisymmetric with respect to the operation of reflection in the plane of the molecule. This limits the number of possible types of orbitals, and hence, of states. In particular, for symmetry  $D_{4h}$  the only possible orbitals are  $a_{1u}$ ,  $a_{2u}$ ,  $b_{1u}$ ,  $b_{2u}$ , and  $e_g$  (see, e.g.,<sup>[130]</sup>). For symmetry  $D_{4h}$ , the only possible states permitted by group theory are the non-degenerate even states  $A_{1g}$ ,  $B_{1g}$ ,  $A_{2g}$ ,  $B_{2g}$ , and the doubly-degenerate odd state  $E_u$ . When the symmetry is lowered to  $D_{2h}$ , the  $E_u$  state splits in two:  $B_{2u}$  and  $B_{3u}$ , while the even states change symbols:  $A_{1g}$  and  $B_{1g}$  go over into  $A_{1g}$  and  $A_{2g}$ , while  $B_{2g}$  goes over into  $B_{1g}$ . Figure 18 illustrates what has been said. The signs "+" and "-" indicate the sign of the wave function.

The ground electronic state of the porphyrins, as with other classes of compounds, must be totally-symmetric ( $A_{1g}$ ). Using the table of direct products (see, e.g.,<sup>[136]</sup>), and taking into account the possible types of symmetry of  $\pi$ -electron states, we can easily derive the following selection rules for the porphyrins. The only transitions allowed in absorption are those to the degenerate  $E_u$  states (for symmetry  $D_{4h}$ ) and to the  $B_{2u}$  and  $B_{3u}$  states (for symmetry  $D_{2h}$ ). The moments of the transitions  $A_{1g}-B_{2u}$  and  $A_{1g}-B_{3u}$  are mutually perpendicular. Correspondingly, Fig. 18 indicates the states for which transition from the



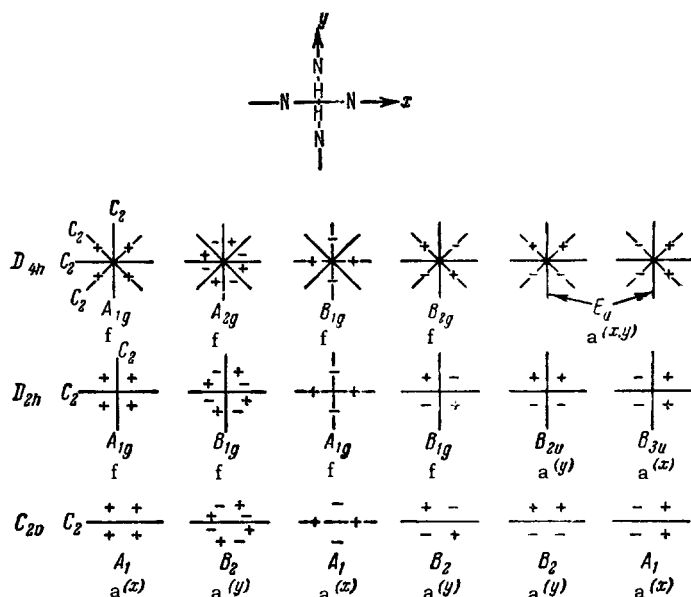


FIG. 18. Symmetry types of the possible  $\pi$ -electron states of the porphin ring.

ground state is allowed by the letter  $a$ , and those forbidden by the letter  $f$ . The polarizations of the transitions are also indicated there. In the case of symmetry  $C_{2v}$  (dihydroporphin), all the transitions forbidden for symmetry groups  $D_{4h}$  and  $D_{2h}$  are allowed, in line with the absence of a center of symmetry.

The experimental data indicate that the allowed transition in the metalloporphyrins and doubly-charged porphyrin ions corresponds to the Soret band. According to what has been said above, this band must be assigned to the transition  $A_{1g}-E_u$ . The small change in the form of this band when the symmetry is lowered means that the states  $B_{2u}$  and  $B_{3u}$  resulting from splitting of the doubly-degenerate  $E_u$  state are close in energy. Apparently, the Soret band of the neutral porphyrin molecules corresponds to two allowed transitions which are close in frequency, and have mutually-perpendicular orientations, in agreement with the polarization spectrum.

As has been noted, in the metalloporphyrins and the porphyrin cations, the lowest excited state is also doubly degenerate. Correspondingly, the long-wavelength transition ( $A_{1g}-E_u$ ) here should be allowed by the selection rules for symmetry  $D_{4h}$ . Hence, the low intensity of band I in this case cannot be explained by a selection rule forbidding the transition on grounds of symmetry, and we must have recourse to other arguments. In particular, Simpson used for this purpose the idea of transitions being "forbidden by the angular momentum." Without going into an analysis of the views of various authors on this problem, we should note that in annular conjugated systems there are factors which greatly weaken transitions which are not forbidden by symmetry. Analogous arguments can also be adduced for symmetry  $D_{2h}$ ; the relatively low intensity of bands I and III may be due to the same factors.

Here, the assumption that the forbidden character does not involve the symmetry of the molecules is also confirmed by a comparison of the absorption and luminescence spectra of porphin and tetrazaporphin. The intense absorption bands of tetrazaporphin are related to bands I and III of porphin, since successive substitution of the bridge carbon atoms by nitrogen atoms increases the intensity of these bands, but hardly alters their positions. When a metal is introduced, the intense absorption bands of tetrazaporphin belonging to the allowed transitions  $A_{1g}-B_{2u}$  and  $A_{1g}-B_{3u}$ , whose oscillators are mutually-perpendicular, merge into one band having planar oscillator. This analogy shows that the electronic excited states do not differ in symmetry type in the two cases. Hence, in the case of porphin, the transitions are not forbidden by symmetry.

The necessity of adopting a planar oscillator as the model for band II of the neutral porphyrin molecules indicates the presence of two equally-probable transitions,  $A_{1g}-\bar{B}_{3u}$  and  $A_{1g}-\bar{B}_{2u}$ , responsible for this band (the bar over a symbol indicates an electronic-vibrational wave function). An analysis of the direct products for the symmetry groups of  $D_{2h}$  shows that such states can arise by excitation of vibrations  $\alpha_{1g}$  and  $\beta_{1g}$ . Thus, the electronic spectra of the porphyrins exhibit the totally-symmetric vibration  $\alpha_{1g}$ , which does not change the oscillator direction, and the non-totally symmetric vibration  $\beta_{1g}$ , which gives a transition oriented perpendicularly to the 0-0 transition. The equality of the X- and Y-components of the electronic-vibrational bands (formation of a planar oscillator), which is observed experimentally, indicates that these vibrations are manifested equally in the spectrum.

However, as is known, the application of the Franck-Condon principle to complex spectra requires the pre-

ferential appearance in the spectrum of the totally-symmetric vibrations. To avoid this contradiction, we must take into account the quasi-forbidden nature of the electronic transitions in the porphyrin molecules.

As is known, the vibrational structure of forbidden transitions results from the dependence of the matrix element of the dipole moment of the transition on the nuclear coordinates.<sup>[136,137]</sup> For small nuclear displacements, the moment of the transition can be expanded in series in terms of the normal coordinates:

$$D = D_0 + \sum_i D_i q_i + \sum_{i,k} D_{ik} q_i q_k + \dots,$$

where  $q_i$  is the normal coordinate giving the value of the displacement in the  $i$ th normal vibration. If  $D_0 = 0$  (forbidden transition), the vibrational bands will nevertheless appear in the spectrum, owing to the superimposition of the non-totally symmetric vibrations through the terms  $D_i q_i$  determining the intensity and polarization of the transitions. That is, the non-totally symmetric vibrations remove the rule forbidding the transition by destroying the symmetry of the equilibrium configuration. In order that the coefficients  $D_i$  should not vanish, the electronic-vibrational wave function must have the transformation properties of one of the states to which the transition is allowed.

For the porphyrins,  $D_0$  is not zero, but nevertheless is very small (especially for porphin). Thus, the terms  $D_i$  must play an essential role. In this case, the mechanism of participation of the vibrations in the electronic-vibrational transitions differs little from the case of strictly forbidden transitions: the vibrations perturb the system and relax the selection rule through distorting the equilibrium configuration.

The totally-symmetric and non-totally-symmetric vibrations appear in the spectra to an equal extent because both types of vibrations here play the same role as a perturbing factor relaxing the quasi-forbidden character of the transition.

Among the possible types of  $\alpha_{1g}$  vibrations, those most likely to appear in the spectrum are those shown in Fig. 19, which resemble in form the  $\beta_{1g}$  vibrations.\* An attempt to estimate the intensities of the X- and Y-components in the absorption spectra of the porphyrins in band II actually indicates that these components may be equal.<sup>[58]</sup>

Thus, the hypothesis that bands II and IV in the absorption spectra of the porphyrins are of vibrational origin, just as is band II in the luminescence spectrum, agrees well with experiment. Unfortunately, we cannot at present explain quantitatively the equality of the X- and Y-components in the cited absorption and emission bands, since we do not know the exact form of the relation of  $D$  to the vibrational coordinates.

\*Interestingly, the vibrations which relax the selection rule in the benzene molecule are of similar form, according to Craig.<sup>[136]</sup>

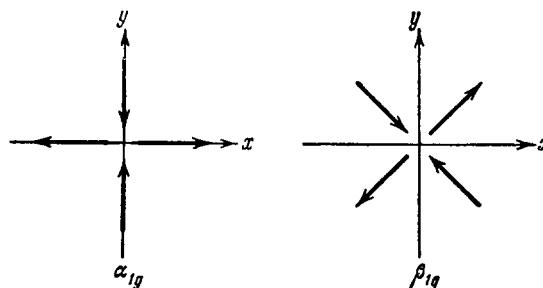


FIG. 19. Probable forms of the vibrations manifested in the electronic spectra of porphyrins.

The group-theoretical discussion given above of the experimental facts permits us to interpret the absorption and luminescence spectra of the porphyrins as follows. Bands I and III in the absorption spectrum belong to distinct electronic transitions. Bands II and IV in the absorption spectrum and band II in the emission spectrum correspond to electronic-vibrational transitions, with the totally-symmetric and non-totally-symmetric vibrations manifested to an equal extent in the spectrum. In line with all that has been said above, the diagram of levels of the porphyrin molecules has the form shown in Fig. 20. The Soret band corresponds to a separate electronic transition.

We must discuss briefly the spectral types of the porphyrins as classified by Stern.<sup>[41]</sup> As has been mentioned, of the 24 possible types of intensity distribution in the four-banded spectra of the porphyrins proper, only three are observed: the "etio type," the "phyllo type," and the "rhodo type." This fact, though amazing at first glance, can be easily explained by the fact that the optical transitions in the porphyrin molecules occur between levels of the porphin conjugated system which are somewhat affected by the side-chain substituents. In investigating the problem of the spectral types, we must start from the spectrum of porphin, in which bands I and III are weak, while bands II and IV are relatively intense, band IV being appreciably stronger than band II. Above, we related this spectral type (the "phyllo type") to the quasi-forbidden character of the electronic transitions and to the special role of the vibrations as a perturbing factor relaxing the selection rule. When side-chain substituents are introduced, the intensities of bands II and IV change little (the types of vibrations are maintained), but bands I and III change more markedly in intensity, since these structural changes in the molecule act as a particular type of perturbation. Thus we get the variety of spectral types. Interestingly, in view of the fact that all symmetrically-substituted porphyrins have "etio-type" spectra, while porphin itself has a "phyllo-type" spectrum, the opinion has been expressed in the literature that the spectrum of porphin shows some sort of anomaly. Of course, the transition from the "phyllo type" to the "etio type"

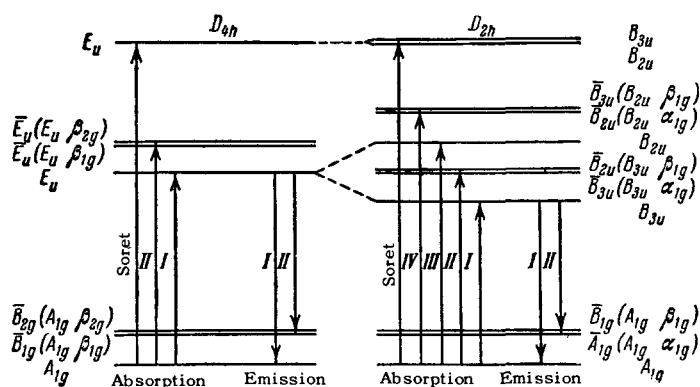


FIG. 20. Energy-level diagram of the porphin molecule.

on symmetrical substitution is actually quite natural, since the electronic transitions are not forbidden by symmetry. The existence of the spectral types of porphyrins cannot be quantitatively explained at present, but seems natural, in view of the quasi-forbidden nature of the long-wavelength transitions. Thus, in the last analysis, the existence of the spectral types involves the weakness of the interaction of the side-chain substituents with the porphin ring system. Under stronger influences, e.g., hydrogenation of pyrrole rings or aza-substitution, the spectrum changes considerably more strongly in character.

This discussion shows that two excited states of the porphin ring are manifested in the electronic spectra in the case of symmetry  $D_{4h}$ . These states are doubly-degenerate, and belong to symmetry type  $E_u$ , the long-wavelength transition being quasi-forbidden. We might say that an analysis of the experimental data shows that the model of "free electrons" in a closed circular ring can be applied qualitatively to the case of the porphyrins. We recall that in this model (of symmetry  $D_{\infty h}$ ), the highest filled orbital is doubly-degenerate and has the form  $ae^{\pm 4i\varphi}$ . For a real symmetry  $D_{4h}$  it splits into two orbitals of symmetries  $a_{1u}$  and  $a_{2u}$ , which do not form a degenerate doublet. The qualitative agreement between the pattern expected for "free electrons" in a circular ring and that observed experimentally can be interpreted as a coincidence of the energy of the  $a_{1u}$  and  $a_{2u}$  orbitals in the porphin ring system (accidental degeneracy). This hypothesis had been advanced previously by Gouterman,<sup>[106]</sup> and has proved useful in interpreting the electronic spectra of the metalloporphyrins.<sup>[58]</sup> At the present time, the best model of the excited states of the porphin molecule is the Simpson-Platt-Gouterman model, which takes into account the configurational interaction between the two excited states of symmetry  $E_u$ , which result from transitions from the  $a_{1u}$  and  $a_{2u}$  orbitals to the  $e_g$  orbital. This model makes it possible to describe correctly a number of spectroscopic properties of the porphyrins, in particular the effect of side-chain substituents on the absorption spectrum.<sup>[81]</sup>

However, we must emphasize again that the current methods of quantum chemistry do not permit the reliable determination of the properties of the electronic states of such complex systems as the porphyrins by calculation. The results of calculations are often ambiguous and depend strongly on the values of the arbitrarily chosen parameters. Only a joint analysis of the experimental data and the theoretical calculations can provide more or less reliable results. A wrong analysis of the experimental data with a satisfactory theoretical model will lead to wrong conclusions. We shall give two examples. A recent paper by Rackow<sup>[139]</sup> based on a model of 18 "free electrons" in the inner ring of 16 bonds states that the two-banded spectrum of the metalloporphyrins involves the removal of the degeneracy of the lowest excited state owing to low symmetry, while the four-banded spectrum corresponds to different NH-isomers. As follows from what has been stated above, these hypotheses do not correspond to reality. In the paper of Bär, Lang, Schnabel, and Kuhn<sup>[120]</sup> cited above (Sec. 6), the conclusion was drawn that the two fluorescence bands of the porphyrins and metalloporphyrins belong to different forms of the molecules; these authors<sup>[120]</sup> also do not deny the possibility that the four-banded absorption spectrum can belong to different NH-isomers. They based the first hypothesis on the absence of a third fluorescence band. [According to the Franck-Condon principle, when  $D(q) = D_0 = \text{const.}$ , if band I is most intense, then the band intensities will be related as  $1 : a : a^2/2! : a^3/3! \dots$ .<sup>[140]</sup> Now, for the porphyrins,  $J_{II}/J_I = 0.7$ ; thus we should observe a progression  $1 : 0.7 : 0.25 : 0.06 \dots$ .<sup>[120]</sup>] A further basis was the difference in the polarization characteristics of bands I and II of the fluorescence spectrum (in the metal-free compounds). In order to explain the independence of the fluorescence spectrum of  $\lambda_{\text{excit}}$ , the authors<sup>[120]</sup> had to assume that, after excitation, equilibrium is rapidly established between the two hypothetical forms. It was shown above that the spectra of the porphyrins exhibit both totally-symmetric and non-totally-symmetric vibrations, with each type of vibration playing a particular role as a perturbing factor. This permits

us to explain not only the "planar oscillator" in the vibrational bands, but also the marked deviation of the intensity distribution of the bands from the Franck-Condon distribution. The hypotheses of the German authors [120] therefore seem completely ungrounded.

In closing this section, we shall discuss the problem of the effect of hydrogenation of the pyrrole rings on the spectra. The strengthening of the long-wavelength absorption band and its shift to longer wavelengths in the series porphin-dihydroporphin-tetrahydroporphin were originally interpreted by Rabino-witch [141] in terms of the appearance of a new excited level upon hydrogenation of each pyrrole ring. Later, Platt [111,142] showed, however, that this effect can be interpreted as a perturbation of the original levels of the porphin system. Later, Seely [123] performed some molecular-orbital calculations for porphin systems with differing degrees of hydrogenation, and showed that the molecular orbitals of the hydrogenated porphyrins resemble the orbitals of porphin in electron-density distribution. Gouterman [106] has used Seely's results, but introducing the correction that the  $a_{1u}$  and  $a_{2u}$  orbitals for porphin should be equal in energy, and that the calculated frequency of the long-wavelength transition should agree with the experimental value. As a result, he obtained qualitative agreement with experiment for the hydrogenated porphyrins. These studies, as well as the analysis of the polarization spectra (see Sec. 6), permit us to assume that hydrogenation of the pyrrole rings does not entail the appearance of new excited levels. However, there is as yet no reliable interpretation of the spectra of the hydrogenated porphyrins. Nevertheless, studies in this field are quite essential, since the elucidation of the properties of the excited states of the molecules of these compounds, especially the chlorins, can give valuable information on the nature of the primary event of photosynthesis.

## 8. SPECTROSCOPY OF ASSOCIATED FORMS OF PORPHYRIN MOLECULES

In the overwhelming majority of cases in living nature, we must be concerned not with isolated molecules of porphyrins, but with complex structures in the form of complexes of pigment molecules with proteins, lipids, and other substances. In a number of cases, it is assumed that the porphyrin molecules, especially chlorophyll in the living leaf, occur in an aggregated state. Here it is of considerable interest to study by spectral-luminescent methods the association of molecules related to chlorophyll and heme under model conditions. The elucidation of the nature of the forces binding the molecules in the complexes, the study of the photochemical characteristics of the molecules forming these complexes, the details of structure of the aggregates, and finally, the dimensions of this type of structure, comprise a set of problems

demanding solution, to which a number of studies have been devoted.

However, interest in the study of the association of porphyrin molecules is not limited to its great biological significance. The characteristics of the association of such complex conjugated heterocyclic systems can provide interesting information on complex formation, and reveal new facets of the phenomenon.

As a rule, association of molecules occurs in solutions at high concentrations. A very important sign of molecular association in solutions is a change in the absorption spectrum, and in some cases, in the luminescence spectrum. As a rule, these changes consist in the appearance of an additional absorption peak on the short-wave side of the long-wavelength absorption band; the intensity of this new peak depends greatly on the concentration and the temperature. The additional peak ordinarily is due to dimers. Further increase in the degree of association of the molecules does not produce such marked changes in the absorption spectra. As a rule, the other absorption bands do not undergo appreciable changes.

At present, most investigators are inclined to think that the attractive forces between the molecules in association are of the van der Waals type, [143] and involve the interaction of the  $\pi$ -electrons of the molecules. Besides, the study of the association of molecules having regularly varying bond lengths in their conjugated systems indicates that an increase in the number of  $\pi$ -electrons is accompanied by an increase in the tendency of the molecules to form complexes.

Most porphyrins are insoluble in the solvents favoring molecular association. Hence, the following method is applied. The compounds to be studied are dissolved in polar solvents (alcohols, acetone, etc.) in appreciable concentrations, and then one adds a certain quite definite amount of water or some other solvent which does not dissolve porphyrins but is highly miscible with the fundamental solvent. Under these conditions, one can obtain absorption spectra for solutions with varying degrees of association. [144] As an example, Fig. 21 shows the results of such an experiment for pheophytin. As the percent water in the solution increases, the peak of the long-wavelength absorption band is appreciably lowered and shifted somewhat to longer wavelengths. At the same time, a new band appears on the long-wavelength side of the fundamental absorption band. The important point here is the occurrence of an isobestic point, indicating the existence of only two types of entities in the solution. We can assume that dimers have been produced. An essential fact is that the luminescence spectra practically do not change here, but only the overall intensity of the luminescence declines.

A study of the association of chlorophyll molecules under analogous conditions shows a somewhat different pattern of spectral-luminescent manifestations of molecular association, in spite of the very similar structure

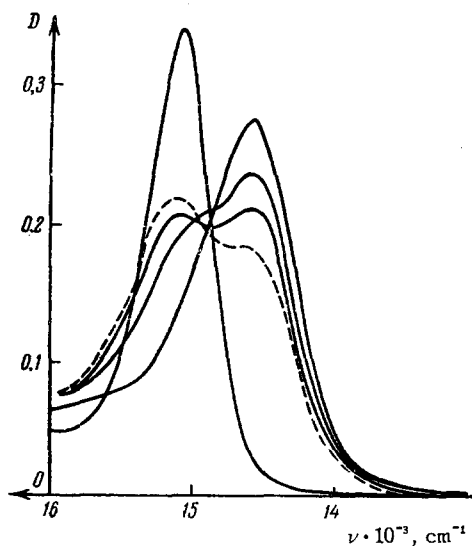


FIG. 21. Spectroscopic manifestation of association of pheophytin molecules.

of the molecules. [145,146] The maximum of the absorption band for the associated molecules is hardly displaced from that of the absorption spectrum of the monomers (Fig. 22). On the other hand, the long-wavelength absorption band undergoes an appreciable lowering and considerable broadening. Perhaps in this case the broadening of the absorption band involves light scattering by the fine colloidal particles which are formed. At least, the interaction of the  $\pi$ -electron clouds of the molecules is considerably less in this case than in that of pheophytin, and this indicates that the mechanism of association in the chlorophyll case is essentially different.

Apparently, molecular association is responsible for the phenomenon of activation of the fluorescence

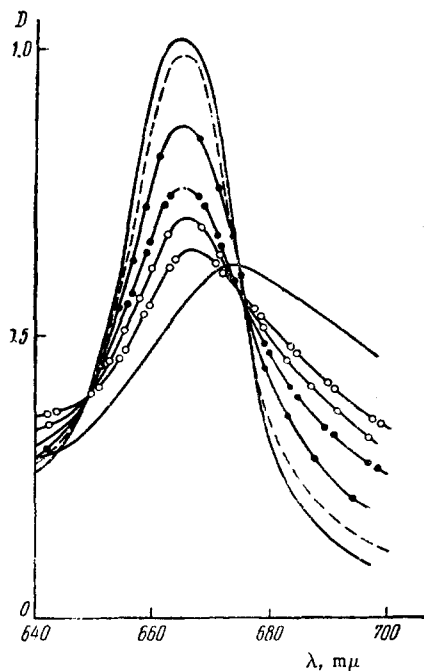


FIG. 22. Spectroscopic manifestation of association of chlorophyll molecules. [145]

of chlorophyll. [108,109] If one prepares with great precautions solutions of chlorophyll in carefully purified dry non-polar solvents, the absorption spectrum turns out to differ from the ordinary spectrum. These solutions are not fluorescent. The addition of small amounts of polar substances (water, alcohols, amines, etc.) causes luminescence to burst forth. Mg-phthalocyanine behaves similarly. Other porphyrins and metalloporphyrins do not show the phenomenon, nor does pheophytin. As has been stated (see Sec. 5), Evstigneev [110] has suggested an explanation according to which the free monomeric molecule of chlorophyll can fluoresce, but non-luminescent aggregates are formed in pure non-polar solvents. The activation of luminescence is explained by disaggregation through the action of the polar molecules.

Jacobs and his associates [147-149] have obtained very interesting information throwing light on the process of association of porphin-type molecules by studying the properties of chlorophylls, pheophorbides, etc. in the form of crystals, colloids, and monolayers. Under certain conditions, ethylchlorophyllide crystallizes to give single crystals of various dimensions. The absorption spectrum of these single crystals is shifted with respect to those of solutions by about  $60 \text{ m}\mu$ . The data obtained are closely similar to the results described above for pheophytin. While the conditions for crystallization of pheophytin differ from those for ethylchlorophyllide, the phenomena which take place with these two related substances apparently have much in common.

The porphyrins proper show a considerably greater tendency to associate. [150] The most characteristic changes here are those in the luminescence spectra (Fig. 23). As glycerol is added to the solution, the first luminescence band of porphyrin (peak at  $635 \text{ m}\mu$ ) gradually decreases in intensity. The same changes also take place in the second emission band ( $703 \text{ m}\mu$ ). At the same time, a new band with a peak at  $676 \text{ m}\mu$  appears and grows. The change in the luminescence spectrum accompanied by simultaneous changes in the absorption spectrum indicates that the aggregates

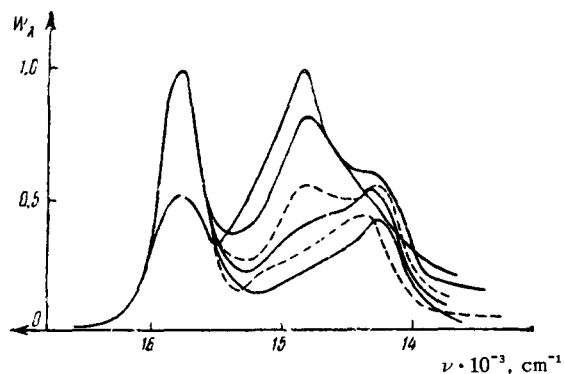


FIG. 23. Changes in the luminescence spectra upon association of protoporphyrin molecules. [144]

formed are luminescent. Since we do not observe a correlation between the changes in the absorption and luminescence spectra, we can naturally assume that aggregates of different constitution have different fluorescent capabilities.

Important facts permitting us to ascertain the occurrence of molecular association, rather than other physico-chemical changes in the solution, are: the temperature-dependence of the absorption and luminescence spectra, the variation in the fluorescent quantum yield with increase in the relative fraction of polymers in the solution, and also the changes in the lifetime of the excited state accompanying the formation of aggregates. The results of a study of the temperature-dependence of the absorption spectra of pheophytin are given in Fig. 24. An increase in the temperature of the solution from 20° to 75°C leads to an almost complete disappearance of the absorption band of the aggregates. The dissociation energy of pheophytin in ethanol-water mixtures determined from the temperature-dependence of the spectra is 2.5 kcal/mole. [144]

The results of a measurement of the quantum yield of luminescence (Fig. 25) show that this characteristic of the emission of the molecules is affected consider-

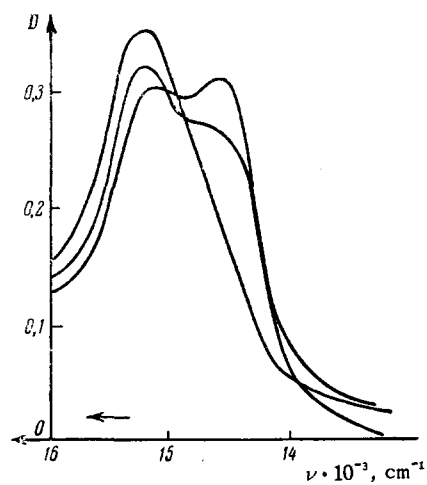


FIG. 24. Temperature-dependence of the absorption spectra of pheophytin.

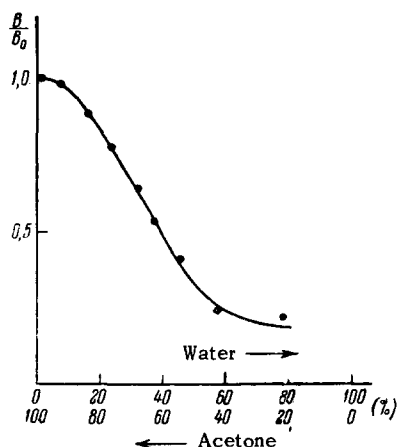


FIG. 25. Relation of the quantum yield of luminescence of pheophytin to the solvent composition. [144]

ably by the addition of a second solvent component to the solution. The luminescence yield of pheophytin decreases by half upon addition of 30–40% water to the solution, and drops almost to zero with 60–70% water. Analogous changes in the quantum yield are also observed for other compounds. On the other hand, the changes in the quantum yield are less pronounced for solutions in mixtures in which the second component is not water, but another solvent. A system in which water is one of the components is more favorable for molecular association than a system containing glycerol.

It is essential to note that the quantum yield of binary solutions of porphin-type compounds decreases appreciably with decreasing temperature. This result, though paradoxical at first glance, obviously involves the formation of polymers, and is an essential sign of the association of molecules.

The relation of the quantum yield for the porphyrins proper in binary solvents to the solvent composition shows a number of peculiarities. [150] In line with the fact that the aggregates in this case can luminesce, the quantum yield changes little in the first stages of association, although here the molecules have a considerably greater tendency to associate. Other conditions being equal, the solutions of porphyrins contain a larger fraction of associated molecules than do the other compounds of this class. Thus, when the ratio of components of the solvent is 3 : 2, the relative quantum yield is still practically unity, whereas in the case of chlorophyll under the same conditions and with the same ratio of components, the yield has decreased by more than 25%. In all probability, this difference indicates that the fluorescent aggregates of protoporphyrin (possibly dimers) show a considerable quantum yield, approaching that of the monomers. A further increase in the glycerol content of the solution results in a sharp drop in the luminescence yield. This latter fact confirms the stated assumption that the high-order aggregates are not fluorescent.

The idea of invoking the concept of molecular association to explain quenching of luminescence as the concentration increases is due to Stenger. [151] As a rule, three fundamental processes can occur in solutions at high concentrations to reduce the quantum yield of luminescence [152]: a) quenching due to inductive migration of energy from monomer to monomer, b) quenching due to inductive migration of energy from monomers to aggregates, and c) quenching due to inactive absorption by non-luminescent aggregates.

In the present case, the concentration of the dissolved molecules in the solutions was so small that the first type of quenching could not occur.\* It is

\*Experiment [153] shows that in chlorophyll-type compounds, concentration quenching begins at a concentration of the order of  $2 \times 10^{-3}$  g/cm<sup>3</sup>.

more complicated to distinguish between the second and third types of quenching, since the conditions are very favorable for both types of quenching. Further facts are needed to solve this problem.

According to the theory of migration of excitation energy from molecule to molecule, including migration from monomers to polymers, the lifetime of the excited state will vary in proportion to the change in the quantum yield.<sup>[154]</sup> In the presence of molecular association, this proportionality is practically never observed. As a rule, the lifetime of the excited state under conditions of association decreases considerably more slowly than the quantum yield. To obviate this difficulty, Levshin<sup>[155]</sup> has introduced into the interpretation the probability of inactive absorption of excitation energy by polymers. Thus, the extent to which the changes in the quantum yield and the lifetime deviate from proportionality is a measure of the participation of these two phenomena in the quenching process.

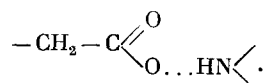
Fluorometric measurements of the lifetime of the excited state were made with various ratios of the components of the solvent in order to ascertain the role of the various types of quenching. The results of the measurements are given in Table II.

Table II

Compound	Solvent	Ratio of components	$\tau \cdot 10^{-9}$ , (sec)	$\tau/\tau_0$	$I/I_0$
Pheophytin a	Ethanol	1:0	5.25	1.0	1.0
	Glycerol	1:1	4.0	0.75	0.33
Chlorophyll a	Ethanol	1:0	4.85	1.0	1.0
	Glycerol	1:1	3.75	0.77	0.45

As we see from the given data, the lifetime of the excited state decreases considerably more slowly than the quantum yield. This fact indicates that inactive absorption by polymers plays an appreciable role in the total quenching of the the luminescence. Unfortunately, the data obtained are insufficient for a precise quantitative determination of the roles of these types of quenching.

The fundamental literature data on the association of porphyrin molecules<sup>[156,157]</sup> refer to the study of aggregation of molecules in weakly alkaline aqueous media upon increase in concentration. The aggregation is observed only in alkaline solutions in which the dissociation of the NH bonds hasn't yet occurred, but the carboxyl groups are already ionized (unesterified porphyrins were studied). Hence, Blyumenfel'd<sup>[128]</sup> considers that the molecular association is due to the interaction of the ionized COO<sup>-</sup> groups with the NH groups of the pyrrole rings, and proposes the following pattern for the formation of the hydrogen bond:



Since the oxygen atoms of the carboxyl groups are negatively charged, the hydrogen bond should be rather strong.

The experimental data described above were obtained in neutral solutions in which no ionization occurs. Besides, the compounds studied did not contain carboxyl groups. The spectroscopic manifestation of association was identical in both cases. In line with this, the mechanism of formation of aggregates of porphyrin molecules proposed by Blyumenfel'd seems to be at least ungrounded.

A fundamental characteristic of the spectroscopic manifestation of association of porphyrin-type molecules is the fact that the absorption band for the associated form of the molecules is not on the short-wavelength side of the monomer absorption band, but on the long-wavelength side. Apparently, an investigation of the problem by quantum-chemical methods could provide essential information on the association of molecules of various classes. In particular, the "free-electron" method permits us in principle to explain also the appearance of the dimer absorption band on the long-wavelength side of the monomer spectrum.<sup>[158]</sup>

On the basis of the existing data, it does not seem possible to propose a concrete mechanism for the association of porphyrin molecules. However, the existing data indicate that a great variety of association processes take place here, as indicated by the differences in the spectral-luminescent properties of the aggregates for various compounds of this class. If we take into account the existing data on the conditions for crystallization of chlorophyll a, pheophytin a, and certain other compounds of this class, we can advance a very well-grounded hypothesis on the structure of the polymers under the given conditions. In fact, the experiments of Jacobs, Holt, Vatter, and Rabinowitch,<sup>[147-149]</sup> as well as those of Belavtseva, Vorob'eva, and Krasnovskiĭ,<sup>[159]</sup> have shown that chlorophyll and pheophytin can be obtained in crystalline form under certain conditions. Here, the crystallization of chlorophyll requires the presence of water molecules which take part in the formation of the crystals, whereas pheophytin crystallizes well in the absence of even traces of water. The forms of the crystals of these compounds were found to differ. If we take into account these data, which were obtained by x-ray diffraction, electron diffraction, and electron-microscope methods, we can picture the formation of aggregates as follows. In the case of pheophytin, the molecules contact one another in the association process on the planes of the porphyrin part of the molecule. Here, the  $\pi$ -electron clouds of the molecules interact, causing a shift in the absorption spectra of the associated molecules with respect to those of the monomer molecules. This shift is of the same order of magnitude as for association of typical dyes (about 30 m $\mu$ ). This again confirms the interaction of the conjugated systems of the partner molecules. Probably dimeri-

zation of the molecules occurs here, since the presence of the phytol residue, which is arranged perpendicularly to the porphyrin part of the molecule should hinder the addition of other molecules. The complex can grow to larger dimensions through other mechanisms not involving such strong interaction of the  $\pi$ -electron clouds of the molecules. In line with this, further polymerization does not result in essential changes in the absorption spectra, as was shown above. For chlorophyll, the binding of the molecules in the complexes involves the direct participation of water molecules. Obviously, the water molecules are bound to the central Mg atoms, and do not permit the molecules to approach the distances necessary for strong interaction of the  $\pi$ -electron clouds of the molecules. Correspondingly, the absorption spectra of the aggregates differ less from those of the monomers than in the case of pheophytin.

The molecule of chlorophyllide lacks the phytol residue, and hence in crystallization can show a strong interaction of the  $\pi$ -electron clouds, resulting in large changes in the absorption spectra.

This qualitative picture of the molecular association is highly hypothetical, and requires further development on all sides.

## 9. PARAMAGNETIC RESONANCE OF THE PORPHYRINS

The phenomenon of paramagnetic resonance, which was discovered in 1944 by Zavoiskii, [160] has provided physicists and chemists with a new, powerful tool for learning the properties of matter. Naturally, the paramagnetic-resonance method has been applied to study the porphyrins, since the interest in this class of compounds is steadily increasing. Already more than twenty papers have been published on this problem.

The essence of the paramagnetic-resonance phenomenon consists in the experimental observation of absorption due to transitions directly between the Zeeman sublevels of the ground state of a paramagnetic particle. Obviously, a transition involving absorption can occur here when the quantum of incident radiation is equal to the energy difference between the split levels which is proportional to the value of the applied magnetic field. In the microwave region of the spectrum where paramagnetic resonance is ordinarily studied, it is experimentally more convenient to study the relation of the absorptive power to the magnetic field intensity at a constant frequency of the radiation, rather than to study the frequency-dependence as one does in optical spectroscopy. Electron paramagnetic resonance (EPR) is observed in systems containing uncompensated electron spins. Examples of such a system are paramagnetic ions incorporated into a crystal structure or the molecule of a complex compound, and free radicals. The condition for resonance has the form:  $h\nu = g\beta H$ , where  $g$  is the spectroscopic splitting (Landé) factor, and  $\beta$  is the Bohr magneton.

If the system contains only one unpaired electron, then one resonance maximum appears in the EPR spectrum, in accordance with the resonance condition. This involves the fact that the ground state splits in the magnetic field into only two sublevels having  $m_s = \pm 1/2$ ; the transition between them is allowed by the selection rule  $\Delta m_s = \pm 1$ . If the spin of the system is greater, several sublevels are produced, the only allowed transitions among them being those with  $\Delta m_s = \pm 1$ . Owing to the interaction between the electrons, the spacings between the corresponding levels will differ somewhat, and we can observe in the EPR spectrum the so-called "fine structure." Hyperfine structure arises from the interaction of the electron spin with the nuclear spin. In studying the electronic structure of chemical compounds, the extra hyperfine structure due to interaction of the electron spin with the spins of the surrounding nuclei is of especial interest. The existence of this extra structure is the most direct experimental proof of the sharing of electrons in the covalent bond and the delocalization of  $\pi$ -electrons in an conjugated chain.

The value of the  $g$ -factor under resonance conditions is determined by the internal fields acting on the paramagnetic ion. When the symmetry is low enough, the  $g$ -factor is anisotropic (it is a tensor). The study of the value and anisotropy of the  $g$ -factor and the determination of the constants of the fine structure and hyperfine structure permit us to obtain accurate information on the electronic structure of the ion.

The EPR studies of the paramagnetic metallophthalocyanines and certain derivatives of hemoglobin and chlorophyll were begun by Ingram and Bennett, [161-172] who studied crystalline samples. Studies have appeared subsequently on the EPR of metalloporphyrins, using viscous and non-viscous solutions. Since the copper ion is very convenient in EPR studies, it is precisely the copper complexes of the porphyrins and related compounds which have been studied best of all. In line with this, we shall discuss the properties of the copper complexes in greater detail, and then briefly discuss the properties of the complexes with other metals.

The  $\text{Cu}^{2+}$  ion has the electronic structure  $3d^9$ ; the total spin of the electron shell is  $1/2$  (one unpaired electron). In abbreviated notation, the experimental results can be represented by the following spin Hamiltonian (for tetragonal symmetry): [173]

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta (H_x S_x + H_y S_y) + A S_z I_z + B (S_x I_x + S_y I_y),$$

where  $g_{\parallel}$  is the value of the  $g$ -factor in a direction along the principal axis of symmetry (i.e., perpendicular to the plane of the molecule),  $g_{\perp}$  is the same in a perpendicular direction, and  $A$  and  $B$  are the hyperfine-structure constants for the stated directions (the terms are omitted which take into account the quadrupole interaction, the direct interaction of the nuclear spin with the external magnetic field, and the extra hyperfine structure).



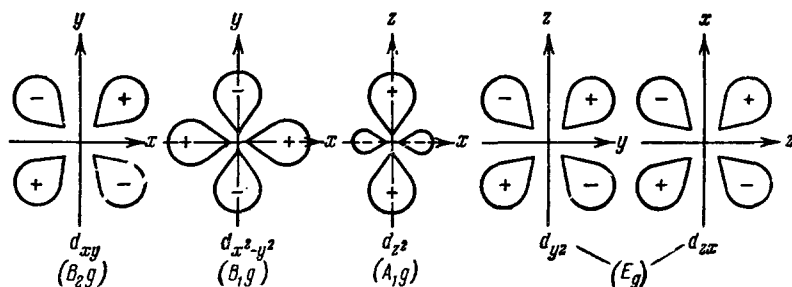


FIG. 27. Symmetry types of the wavefunctions of the d-electrons in an ion of tetragonal symmetry.<sup>[177]</sup>

Even the first EPR measurements of Cu-phthalocyanine crystals<sup>[161]</sup> showed that the values of the g-factor differed markedly from the characteristic values for ionic crystals of copper salts. Therefore, covalent bonding takes place. "Magnetic dilution" of the crystals with Zn-phthalocyanine permitted the resolution of the hyperfine structure due to the spin moment  $I = 3/2$  of the copper nucleus.<sup>[162-163]</sup> The following values were obtained for the spin Hamiltonian coefficients:  $g_{\parallel} = 2.165$ ,  $g_{\perp} = 2.045$ ,  $A = 0.022 \text{ cm}^{-1}$ ,  $B = 0.003 \text{ cm}^{-1}$ .

The extra hyperfine structure due to the nitrogen atoms of the porphin ring was not detected in the crystals diluted with Zn-phthalocyanine. However, it was found later in solutions (of low concentrations) of Cu-etioporphyrin,<sup>[174]</sup> and then in Cu-phthalocyanine.<sup>[175,176]</sup> This fact is convincing evidence of the sharing of electrons in the Cu-N bond, i.e., of its covalent character. From the constants A and B, we can determine the probability of finding the unpaired electron near the copper atom (defined as  $\alpha^2$ , where  $\alpha$  is the coefficient of the d-orbital in the molecular orbital occupied by the unpaired electron). The value of  $\alpha^2$  can also be determined from the splitting in the extra hyperfine structure of nitrogen, since this splitting increases as the probability of finding the electron on the nitrogen atoms increases, the latter probability being directly related to  $\alpha^2$  by the normalization condition. Both methods of calculation give practically the same result:  $\alpha^2$  is about 0.75 for the various porphin complexes of copper.

The following diagram of one-electron levels (orbitals) of Cu-phthalocyanine (Fig. 26) has been proposed on the basis of an analysis of the results of the EPR study of Ingram, Gibson, and Schonland.<sup>[172]</sup> As is known, in the Ligand field, the orbital degeneracy of the d-electrons is removed, and the d-orbitals belonging to different symmetry types (Fig. 27) for the given symmetry group have different energies.\* This is illustrated on the left-hand side of the diagram. The eight  $\sigma$ -electrons of the anion are shown on the right.

\*The ligand field can be represented as a field of negative charges arranged at the sites of the atoms forming bonds with the metal. Hence, the d-orbitals having the largest energy are those which overlap most with the hybrid  $\sigma$ -orbitals of the ligand, and vice versa (see, e.g.,<sup>[177]</sup>).

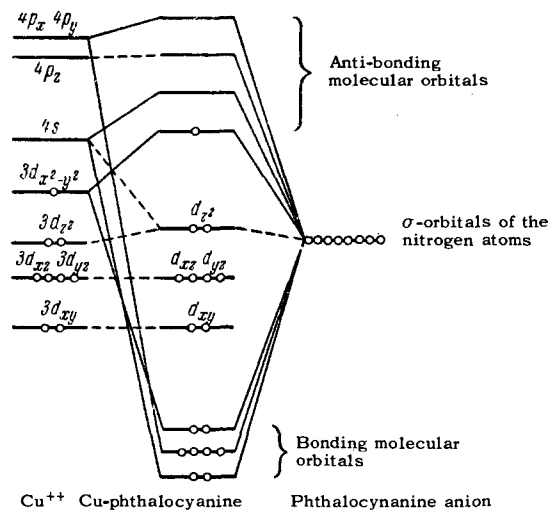


FIG. 26. Diagram of the single-electron levels of Cu-phthalocyanine<sup>[172]</sup> (—o— =  $d_{x^2-y^2}$ ).

The formation of the chemical bonds with the ring can be described by means of a molecular-orbital representation; this is illustrated in the central part of the diagram. In the formation of the chemical bonds, the molecular orbitals arise from the valence orbitals of the copper atom ( $3d_{x^2-y^2}$ ,  $4s$ ,  $4p$ ) and linear combinations of the  $\sigma$ -orbitals of the ligand having the appropriate symmetries. Thus bonding and antibonding (or unstabilizing) molecular orbitals are formed. If the bond is not purely covalent, the atomic orbitals of the ligand play the predominant role in the formation of the bonding orbitals, and conversely, the metal orbitals predominate in the antibonding orbitals. The diagram shows the formation of three bonding orbitals (one of which is doubly-degenerate), filled with eight  $\sigma$ -electrons. The  $3d$ -orbitals of copper other than the  $d_{x^2-y^2}$  overlap weakly with the  $\sigma$ -orbitals of the ligand, and undergo only insignificant changes upon formation of the chemical bonds (unless  $\pi$ -bonds are formed). Of the nine d-electrons of the copper atom, eight occupy the hardly-changed d-orbitals, and one occupies the antibonding molecular orbital  $d_{x^2-y^2}$  ( $B_{1g}$ ). The order of arrangement of the d-orbitals in the level diagram of the complex can be established by the following reasoning. The  $d_{x^2-y^2}$  ( $B_{1g}$ ) orbital has the highest energy; this follows not only from general considerations, but also agrees well with the experimental value

of the  $g$ -factor. The delocalization of the electron in this orbital is also indicated by EPR data, as has been stated above. The order of the other orbitals cannot be established so firmly. We might assume that the energy of the  $d_{z^2}$  orbital will be higher than those of the  $d_{xz}$ ,  $d_{yz}$ , and  $d_{xy}$  orbitals, since in the cobalt complex of phthalocyanine, EPR data indicate that the unpaired electron occupies the  $d_{z^2}$  orbital (the  $\text{Co}^{+}$  ion has the electronic configuration  $3d^7$ , and in its complexes the seven electrons occupy the lowest localized orbitals, the unpaired electron going into the orbital having the largest energy among these). Finally, the order of arrangement of the other orbitals has been determined from the value of the  $g$ -factor of the copper complex. Here it was assumed that  $g_{\parallel} = 2 + 8\lambda\alpha^2/E_1$ , and  $g_{\perp} = 2 + 2\lambda\alpha^2/E_2$ , where  $\lambda$  is the spin-orbital interaction constant for the free ion, and  $E_1$  and  $E_2$  are the energy differences between the  $d_{x^2-y^2}$  and  $d_{xy}$ , and between the  $d_{x^2-y^2}$  and  $d_{xz}$ ,  $d_{yz}$  orbitals, respectively. For  $\alpha^2 = 0.79$ , the following values were obtained:  $E_1 = 31700 \text{ cm}^{-1}$ , and  $E_2 = 29000 \text{ cm}^{-1}$ . Thus, the  $d_{xy}$  orbital has the lowest energy. The level diagram (Fig. 26) has been drawn on the basis of this reasoning.<sup>[172]</sup>

The values of the  $g$ -factor measured for Cu-etio-porphyrin<sup>[174]</sup> hardly differ from those given above for Cu-phthalocyanine. The latter differ somewhat from the values of the  $g$ -factor of Cu-phthalocyanine in concentrated  $\text{H}_2\text{SO}_4$  ( $g_{\parallel} = 2.18$ <sup>[175,176]</sup>). This is not remarkable, since undoubtedly changes take place in the electron cloud of the molecule upon solution in concentrated  $\text{H}_2\text{SO}_4$ . This is indicated by the marked changes in the spectrum of the  $\pi$ -electron system (according to our measurements, the long wavelength absorption band is shifted here by  $100 \text{ m}\mu$  to longer wavelengths).

If the values of  $E_1$  and  $E_2$  could be found from independent data,\* then, knowing the value of  $\alpha^2$ , we could use more accurate formulas for  $g_{\parallel}$  and  $g_{\perp}$ , and get more detailed information on the structure of the electron shell of the copper atom in the porphin ring. However, it is not permissible to take the values of  $E_1$  and  $E_2$  from the optical spectrum, as Roberts and Koski<sup>[174-175]</sup> have done, since the bands in the spectra of the metalloporphyrins correspond to transitions between the levels of the  $\pi$ -electrons of the porphin ring, rather than those of the  $\pi$ -electrons of the metal (see above, Sec. 7). The above statements are further confirmed by the following argument: if the value of the  $g$ -factor were determined by the spacing between the levels manifested in the optical spectra, the  $g$ -factors

of Cu-phthalocyanine and the Cu-porphyrins would differ considerably, but this is not found to be so. In our view, it is also impermissible to postulate the values of  $E_1$  and  $E_2$  by analogy with other copper complexes, as Kivelson and Neiman<sup>[178]</sup> have done. The values of  $E_1$  and  $E_2$  which these authors chose led them to the notion of a strong interaction of the electrons in the  $d_{xy}$  orbital with the  $p$ -electrons of the nitrogen atoms, which at the same time form  $\sigma$ -bonds involved in the skeleton of the molecule. Such a  $d$ - $\pi$  bond in the plane of the molecule is actually not proved thereby, since the values of  $E_1$  and  $E_2$  were selected arbitrarily. The diagram proposed by Ingram et al. seems to us to agree better with current knowledge on the interaction of metals with organic ligands. The increase in the energy of the degenerate  $d_{xz}$ ,  $d_{yz}$  orbital can be easily explained by the formation of weak  $d$ - $\pi$  bonds (of the ordinary type, i.e., out of the plane of the molecule). Analogously to the way that the energy of the unpaired electron increases when  $\sigma$ -bonds are formed, the energy of the  $d_{xz}$ ,  $d_{yz}$  ( $E_g$ ) orbital is also increased by  $\pi$ -bond formation with the electrons in the  $\pi$ -orbital of  $E_g$  type.

An interesting result has been obtained for Cu-tetrachlorotetraphenylporphin.<sup>[164]</sup> In this compound the chlorine atoms replace the four hydrogen atoms in the para positions of the benzene rings. An EPR study of crystals of Cu-tetraphenylporphin has shown that the hyperfine structure of the copper is observed, but the extra hyperfine structure of the nitrogen is blurred out (just as in the crystals of Cu-phthalocyanine). When we go to the tetrachloro-derivative, the picture changes sharply: the extra hyperfine structure typical of chlorine appears. Since the values of the  $g$ -factor do not change here, i.e., the copper atom apparently does not interact with the chlorine atoms of neighboring molecules, the authors conclude that the unpaired electron of the copper is delocalized throughout the organic molecule. A parallel study of the infrared spectra has shown that the frequency of the C-Cl stretching vibration depends on the nature of the metal, which can be explained only by a long-range interaction (through the  $\pi$ -electron system<sup>[179]</sup>). However, recently Kivelson and Neiman<sup>[178]</sup> have cast doubt on the correctness of these conclusions, proposing that the extra hyperfine structure in the EPR structure of the tetrachloro-derivative is due to the nitrogen atoms. They made special studies showing that the replacement of the hydrogen atoms on the benzene rings of phthalocyanine by Cl,  $\text{NO}_2$ , and  $\text{SO}_3\text{H}$  groups does not lead to changes in the EPR spectrum (in solution). That is, the probability of finding the unpaired electron on the periphery of the ring is very small. However, we might object that the EPR pattern observed for Cu-tetrachlorotetraphenylporphin differs markedly from that observed for the other Cu-porphyrins under conditions when the extra hyperfine structure of the nitrogen is resolved. The question of the possibility of

\*The optical transitions between the corresponding levels are forbidden by the Laporte rule. However, in certain complexes they appear nevertheless in the form of very weak bands. In the complexes containing porphin rings, these bands are masked by the intense  $\pi$ -electron absorption.

delocalization of the unpaired electron throughout the macrocycle is still open.

The electronic configuration of the  $\text{Ag}^{++}$  ion ( $4d^9$ ) is analogous to that of  $\text{Cu}^{++}$ , and the diagram of formation of molecular orbitals must be the same. The EPR spectrum of Ag-deuteroporphyrin<sup>[180]</sup> exhibits a hyperfine structure due to the nuclear spin  $I = 1/2$  of silver and an extra hyperfine structure due to nitrogen, with  $g_{\parallel} = 2.104$ ,  $g_{\perp} = 2.029$ . Characteristically, the splitting in the extra hyperfine structure is 1.5 times that in the copper complexes of the porphyrins. This indicates a greater covalent character of the bond, the value of  $\alpha^2$  being 0.58 for Ag, as compared with 0.75 for Cu.

The vanadyl ion  $\text{VO}^{++}$ , which has one unpaired d-electron (the electronic configuration of the  $\text{V}^{+4}$  ion is  $3d^1$ ) is convenient for EPR studies. The spin of the vanadium nucleus is  $7/2$ , whereby the EPR spectra of the vanadyl-porphyrins exhibit eight components in the hyperfine structure, with  $g_{\parallel} = 1.948$ ,  $g_{\perp} = 1.987$ . However, the extra hyperfine structure due to nitrogen is absent.<sup>[181,182]</sup> Reference<sup>[182]</sup> suggests the following explanation for the absence of this hyperfine structure: the unpaired electron occupies the  $d_{xy}$  orbital, which has an electron density of zero at the nitrogen atoms (Fig. 27).\*

The magnetic properties of the iron complexes of porphyrins are of especial interest with regard to the great biological importance of hemoglobin and its derivatives. Measurements of the magnetic susceptibility of heme (Fe-protoporphyrin) indicate the presence of four unpaired electrons, as in the free  $\text{Fe}^{++}$  ion. Hemin (FeCl-protoporphyrin) and the ferrihemoglobins show the presence of five unpaired electrons, as in the free  $\text{Fe}^{+++}$  ion. On this basis, the conclusion has been drawn of a "purely ionic" bond in these compounds.<sup>[183]</sup> However, the results of an EPR study permit us to reject this conclusion. While typically ionic ferric salts exhibit five fine-structure components, and the g-factor is about 2, in the ferric porphyrin complexes the g-factor has the values:  $g_{\parallel}$  about 2, and  $g_{\perp}$  about 6,<sup>†</sup> while the fine structure is absent (the hyperfine structure is also absent, since  $I = 0$ ).<sup>[163,165,172,184]</sup> These facts convincingly demonstrate that the state of the iron atom is essentially different from that of the  $\text{Fe}^{+++}$  ion in the ionic compounds. Consequently, the bonds in the porphyrin complexes of iron are not ionic. Probably, the formation of covalent bonds using the 4d orbital without rearrangement of the 3d electrons is energetically favored for iron. The latter electrons maintain their parallel spins, thus giving rise to the paramagnetism of the

\*A study of the diagram of formation of molecular orbitals in this case shows that this orbital must have the lowest energy.

†Interestingly, FeCl-phthalocyanine has a different value,  $g_{\perp} = 3.8$ ,<sup>[163]</sup> while hemin can show various values of  $g_{\parallel}$ , depending on the crystal modification.<sup>[184]</sup>

Fe-porphyrins.<sup>[185,128]</sup> With regard to the EPR studies of hemoglobin derivatives, we might also mention that these studies have served as a basis for determination of the orientation of the planes of the hemes in hemoglobin crystals and the angles between the heme planes and the polypeptide chains, and from these data, the dichroism of the crystals could be calculated.<sup>[167,168,171]</sup>

In closing this section concerning the paramagnetic resonance of the porphyrins, we shall discuss some data on proton magnetic resonance (PMR) spectra obtained very recently. As is known, the effective magnetic field acting on a given nucleus in a molecule differs somewhat from the external field. This screening by the electron clouds differs for nuclei of like atoms which differ in the chemical bonds that they form. This gives rise to the "chemical fine structure" of nuclear magnetic resonance. In such cases, one customarily refers to "chemical shifts."\* The study of chemical shifts, especially in proton resonance, permits us to get valuable information on the structures of organic molecules.

The PMR spectra of porphyrins were first studied by Becker and Bradley,<sup>[187]</sup> who studied six porphyrins in  $\text{CDCl}_3$ . The PMR spectra are characteristic, and easily amenable to interpretation. The essential points are that the resonance for the protons of the CH groups of the methine bridges occurs at magnetic fields lower than usual for CH protons in conjugated chains, while conversely, the central protons show a resonance at higher fields than usual for NH protons. A phenomenon analogous to the former one (a positive shift on the  $\delta$  scale for CH-group protons) had been previously observed in benzene, and ascribed to the influence of the ring current induced in the systems of mobile  $\pi$ -electrons by the external magnetic field.<sup>[188]</sup> The PMR data indicate the existence of an analogous ring current in the porphyrin ring; for the protons inside the ring, this current should give a shift in the opposite direction, as is observed experimentally. An attempted calculation gave a rough qualitative agreement with experiment (the 18  $\pi$ -electrons were assumed to move in a ring of radius 3.3 Å).

A series of studies has been made by some English authors<sup>[189-191]</sup> on the PMR of porphyrins, including porphyrin itself, in the form of dications (in  $\text{CF}_3\text{COOH}$  and  $\text{CF}_3\text{COOD}$ ). The general features of the spectra are the same as in neutral media. They came to the

\*The chemical shift  $\delta$  is defined by the formula  $\delta = 10^6 \times (\text{H}_{\text{standard}} - \text{H})/\text{H}_{\text{standard}}$ , where  $\text{H}_{\text{standard}}$  is the field at which the resonance line appears for a compound chosen as a standard (usually tetramethylsilane), and  $\text{H}$  is the field at which the resonance line appears for the compound being studied. The chemical shift defined thus is measured in parts per million (p.p.m.). It has also been suggested to measure the chemical shift on a scale  $\tau$ , where  $\tau = 10 - \delta$ .<sup>[186]</sup> The  $\tau$  scale is convenient in that all of the commonly observed shifts have the same sign (+), with larger values of  $\tau$  denoting greater screening of the proton.

same conclusion as in [187] on the existence of ring currents. Interestingly, the ring current has less effect on the protons in the  $\beta$ -positions of the pyrrole rings than on the methine-bridge protons. An essential result was the demonstration of the additivity of the effect of side-chain substituents on the chemical shift for the methine-bridge protons, as well as the central protons. Here the shift is determined practically only by the two nearest substituents. The latter fact has the result that the CH (methine bridges) and NH resonance lines split into multiplets in the asymmetrically substituted porphyrins. Abraham [191] has calculated the effect of the ring current on the chemical shifts in porphyrin molecules. He assumed in the calculation (following Pauling [192]) that the emf in the closed circuit is proportional to the area encompassed by the circuit, while the resistance is proportional to the number of bonds. The branching of the currents in the porphin ring was taken into account. The calculated results are 1.5 times as great as the experimentally-observed chemical shifts (when multiplied by 2/3, they agree very well with experiment). In view of the crudeness of the initial assumptions, the author considered the result to be satisfactory. It is of importance that the theory explains naturally the difference in the chemical shifts of the protons of the CH groups of the pyrrole rings and those of the methine bridges. A comparison made between the PMR spectra of coproporphyrin in neutral medium [187] and in acid medium [190] is of interest. On going to acid medium, a positive shift is observed for all the external protons, and a negative shift for the central protons. This is natural, since as was said above, the symmetry of the system is increased in forming the dication, the delocalization of the  $\pi$ -electrons is increased, and hence, the current is increased. According to Abraham's estimate, the current increase by 20% (as judged by the positive shift). We cannot determine the change in the current from the negative shift for the N-protons, since the charge on the nitrogen atoms changes on going to acid medium, and this also affects the value of the chemical shift.

In a study of the PMR spectra of porphyrins in neutral media, Becker, Bradley, and Watson [193] found no difference in the chemical shifts for the protons of methyl groups bound to non-equivalent pyrrole rings. They suggested on this basis that a rapid interconversion of NH-tautomers takes place, resulting in an averaging of the properties of the pyrrole rings. Here, the lifetime of a tautomer is much shorter than 1/200 sec. The problem of the possibility of rearrangement of the protons in the center of the porphin ring was discussed in detail above. The tautomer of symmetry  $C_{2v}$  probably does not exist, but the shift of the protons from one pair of opposite atoms to the other pair is possible in principle. Here, the lifetime of a given configuration having rigidly defined transitions exceeds the lifetime of the excited state (see

Sec. 6). If we could establish from PMR data the exact upper limit of the lifetime of a given configuration, this would permit us to estimate this quantity qualitatively, and perhaps even measure it. However, the conclusions of Becker et al. lack any serious verification, either experimental or theoretical. From the experimental standpoint, one must study the non-equivalence of the pyrrole rings by using the protons directly bound to them, rather than those of methyl groups. From the standpoint of theory, one must take into account the branching of the current in the porphyrin molecule, which is not done in [193].

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