

THE INFRARED SPECTRUM OF PORPHIN

by

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A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of  
the requirements for the  
degree of

DOCTOR OF PHILOSOPHY

June 1954

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Date thesis is presented April 15, 1954

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### ACKNOWLEDGMENT

The author wishes to express his thanks to Professor J. C. Decius for advice and encouragement tendered throughout the course of the work described here.

He also wishes to thank Mr. Richard M. Teeter of the Department of Chemistry and Chemical Engineering of the University of Washington for the contribution of samples of several porphyrins and helpful discussions regarding the porphin synthesis and separation. Dr. David F. Eggers of the same Department supplied blueprints for the potassium bromide window press.

A large part of this work was done with the aid of a grant from Research Corporation and this assistance is gratefully acknowledged.

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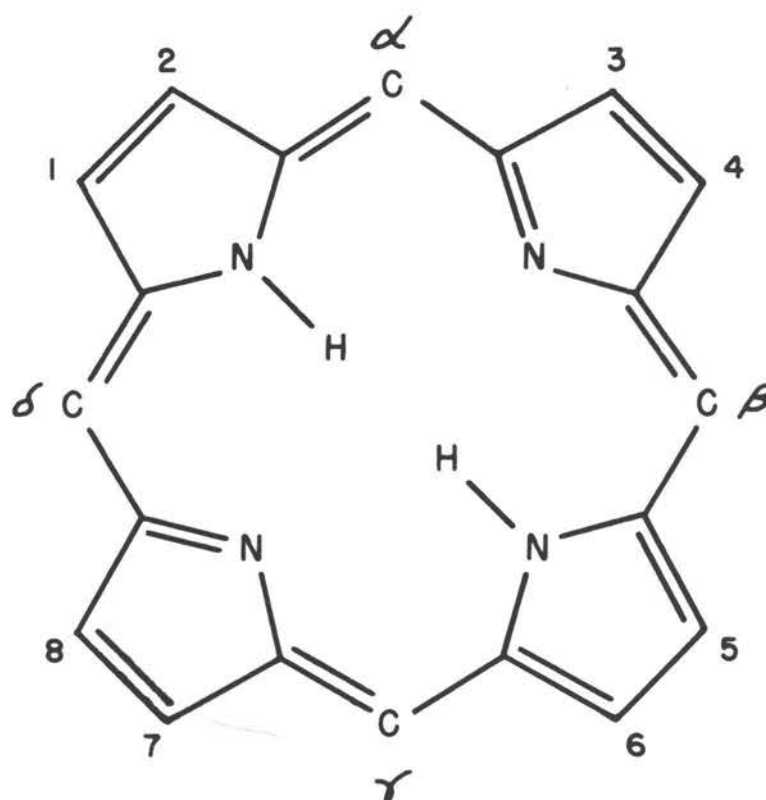
# THE INFRARED SPECTRUM OF PORPHIN

## INTRODUCTION

Infrared spectroscopy has developed into a tool of major importance in the determination of molecular structure. Its approach to this problem varies from the extremely sophisticated, as exemplified by the FG matrix method developed by E. B. Wilson, Jr. to the unabashedly empirical method of characteristic or group frequencies.

The more analytical methods, which lean heavily on group theory, have been restricted in their application to relatively simple molecules. This restriction is not due to any defect in the methods themselves but rather to practical considerations. For larger or less symmetrical molecules the calculations become impractically cumbersome. The method of group frequencies, while not depending on the size or symmetry of the molecule, gives less detailed information about structure. It also suffers from the assumption that the bonding of a particular group changes little from molecule to molecule. While in many cases this is a good approximation, it is by no means strictly accurate and introduces some uncertainty.

Porphin (Figure 1), the subject of this study, occupies a position between the simple and the complex in the spectroscopic sense. Since the porphin molecule contains 38 atoms it should have 108 vibrational degrees of



SUBSTITUENTS

COMPOUND

$\alpha - \delta, 1 - 8$  H

PORPHIN

1, 4, 5, 8 Me  
2, 3, 6, 7 Et

ETIOPORPHYRIN II

$\alpha - \delta$  Ph

TETRAPHENYL -  
PORPHIN

THE PORPHYRIN NUCLEUS

FIGURE I

freedom. This would indicate a spectrum of hopeless complexity. However the results of structural determinations made by the methods of organic chemistry indicate that the porphin molecule is highly symmetrical. In general high symmetry leads to simplicity in the spectrum so that there is a hope, at least, that the application of analytical methods can be made in the discussion of its spectrum.

As the parent compound of the porphyrin series, which includes heme and chlorophyll, porphin is of great interest to the chemist. A sufficiently detailed knowledge of its spectrum would form the basis of calculations which would be of great interest in photosynthesis and the chemistry of combustion processes in the body. Infrared spectroscopy also offers a promising approach to the problem of the location of the inner or imino hydrogens of the molecule, a question which has aroused no little controversy.

## THE CHEMISTRY OF THE PORPHYRINS

Hemoglobin and chlorophyll (10,p.1259-1292) are of unique importance in the economies of the higher animals. Chlorophyll plays an essential role in the fixation of the sun's energy in photosynthesis and is thus ultimately responsible for all our food and a large part of our heat and power. The efficiency of hemoglobin as a transporter of oxygen as well as its versatility in being a transporter of part of the carbon dioxide formed by combustion processes in the body, help make possible the efficient mechanical performance of the higher animals.

Hemoglobin is a conjugated protein made up of heme, a ferrous complex of protoporphyrin; and globin, a water soluble, slightly basic protein. Catalase is another conjugated protein which contains the same heme as hemoglobin combined with a different protein. Catalase has the property of converting hydrogen peroxide to water and oxygen but not the property of combining reversibly with oxygen. This indicates that the physiological properties of iron-porphyrin complexes are largely determined by the nature of the constituent base. Chlorophyll, at least as isolated, contains no protein and has as its metallic constituent magnesium instead of iron. Its chromophoric group is also modified from a porphyrin to a chlorin.



The elucidation of the structure of hemin took place over a period of more than fifty years. Hemin was first crystallized in 1853. Its complete synthesis was described by Fischer and Zeile in 1929. This determination, which will be described only briefly here, offers a striking example of the ingenuity of the organic chemist. Studies of the acidic and basic degradation products of hemin resulted in the identification of a number of pyrroles and dipyrromethenes. A molecular weight determination which indicated that there must be four pyrrole residues in the porphyrin, combined with analytical results indicating the presence of two carboxyl groups, provided a basis for the projection of possible formulas for hemin. It seemed logical to suggest that the pyrrole rings are joined by bridges consisting of a single carbon atom, since all possible combinations of zero and one carbon atom occur in the  $\alpha$ -positions of the pyrrole derivatives isolated, but no two carbon residue was found.

In 1912 Kuster advanced a formula for hemin nearly identical to the one presently accepted. Alternative structures suggested by Willstatter and by Fischer were eventually rejected in favor of the Kuster formula, on the basis of accumulated synthetic evidence.

Structure proofs in the porphyrin series differ from those in other series of organic compounds in that



degradations drastic enough to break the porphyrin nucleus are also drastic enough to cleave the products of the porphyrin fission leaving only small fragments. The method of degradation was thus not capable of establishing the nature of the porphyrin nucleus, much less the relative positions of the side chains. For this reason the synthetic method was resorted to and systematically exploited by Fischer.

The most striking physical characteristic of a porphyrin is its visible absorption spectrum, consisting of four qualitatively characteristic bands. Using the absorption spectrum as a major criterion of success or failure, Fischer was able to achieve synthesis. After this he devised alternative methods for producing the porphyrin nucleus which showed the nature of the linkages in the ring system.

## THE SYNTHESIS OF PORPHIN AND ITS STRUCTURE

After many fruitless attempts Fischer and Gleim succeeded in synthesizing porphin (9,p.157), the parent compound of the porphyrin series, from  $\alpha$ -pyrrolealdehyde. The aldehyde, in the form of its alcohol solution, was introduced into boiling formic acid and the reaction allowed to proceed for 36 hours. Porphin could be isolated from the resulting mixture in very small amounts. Using 20 grams of aldehyde it was possible to isolate only 17 milligrams of crystalline material. The compound was identified by means of its elemental analysis and its visible spectrum. A Zerewitinoff determination indicated the presence of two active hydrogens.

In 1935 Rothmund reported (20,p.2010) that porphyrins were formed when mixtures of pyrrole and solutions of formaldehyde were (a) kept at room temperature for several weeks, (b) heated under reflux for fifteen to twenty-five hours or, (c) heated in a sealed tube to 85°-90° C. for ten to twenty hours. The separation of the porphyrins from the reaction mixture entailed fractionation with hydrochloric acid. The products were identified as porphyrins by means of their visible absorption spectra.

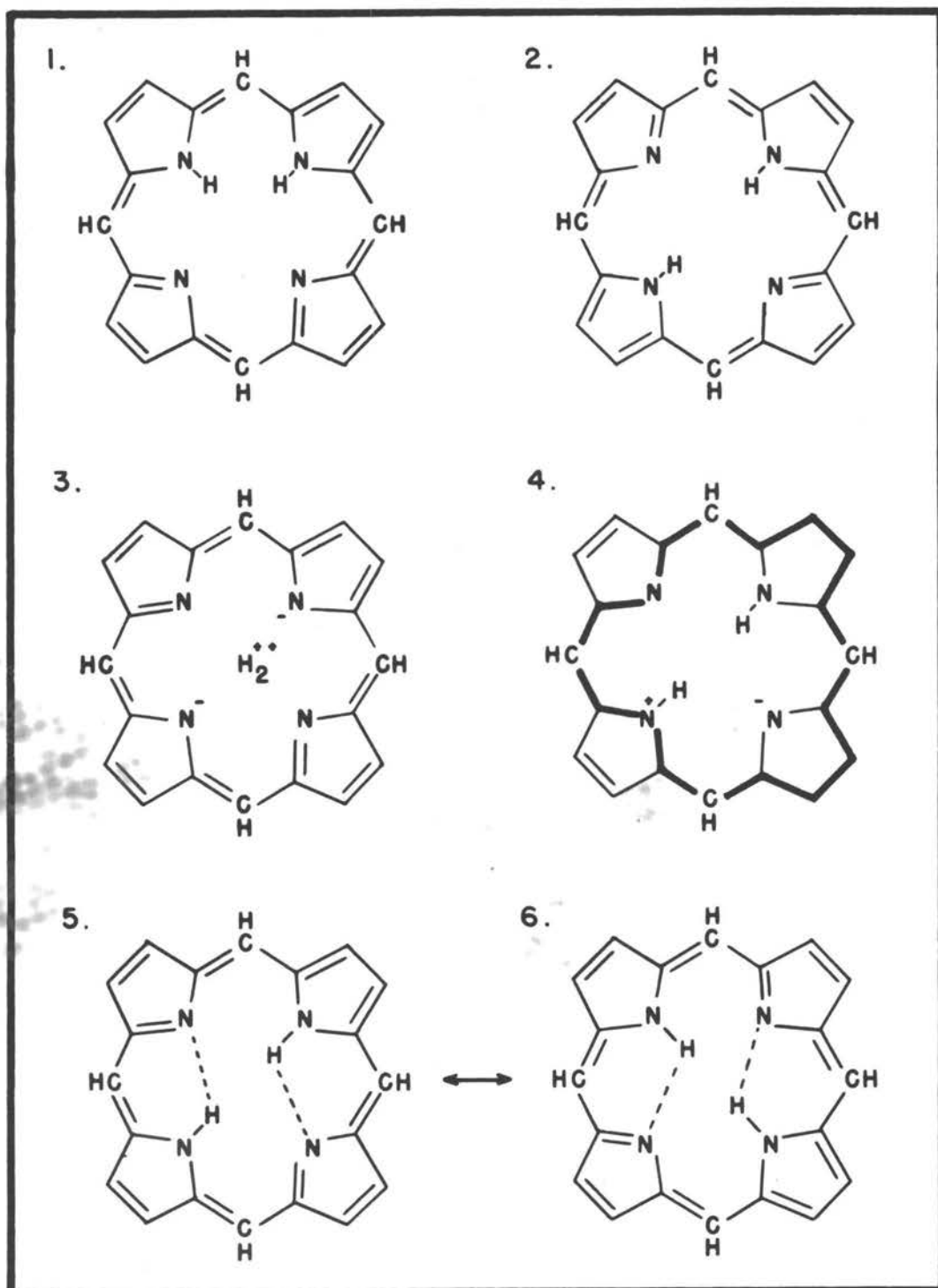
In a later publication Rothmund described (21, p.625) the extension of this method of synthesis to other

aldehydes. The synthesis of porphin was described as an example of the method. The hemin (iron), phyllin (magnesium), and copper complex salts of porphin were prepared. Rothemund observed that if the synthesis with formaldehyde and pyrrole were performed at  $145^{\circ}$ - $155^{\circ}$  instead of  $90^{\circ}$ - $95^{\circ}$ , a material which he described as a porphyrin, resulted, which differed from porphin spectroscopically in the positions of the two main visible absorption bands. These bands were shifted approximately  $100 \text{ \AA}$  toward the red region of the spectrum. The hydrochloric acid number<sup>1</sup> was much lower than that of porphin.

In a more detailed study (22,p.2912) the hydrochloric acid number of the porphyrin obtained at  $140^{\circ}$ - $145^{\circ}$  was determined to be 0.5 as compared to 3.3 for porphin. The elementary analysis checked with that of porphin within the limits of experimental error. An attempt at direct determination of the molecular weights of the two porphyrins met with failure but on the basis of the analytical and spectroscopic data Rothemund concluded that the new porphyrin was an isomer of porphin and suggested the name "isoporphin" for it (Figure 2, 1 and 2).

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<sup>1</sup> The hydrochloric acid number, often used to characterize chlorophyll derivatives, is defined as that percentage concentration of hydrochloric acid which extracts two-thirds of the substance from an equal volume of ether.



STRUCTURAL FORMULAS  
FOR PORPHIN

FIGURE 2



Corwin and Quattlebaum (5,p.1081) pointed out the fact that the acid salts of N-isomeric porphyrins would be "resonance" isomers, i.e., they would correspond to a single structure. As a result N-isomerism would be expected to be detected only if the free bases were fractionated by a procedure not involving acids. The examination of a space model suggested to them the possibility of hydrogen bonding between adjacent secondary and tertiary nitrogen atoms. Corwin and Quattlebaum state "In such a case the predicted N-isomerism would not appear but might give way to another type in which the hydrogen bridges exchanged their partners. Substitution of a functional group for hydrogen would destroy the latter isomerism and create the appearance that the original porphyrins were N-isomers."

Rothemund's conclusion that the two materials which he had isolated were nitrogen isomers also came under fire on another account. It was suggested (17, p.101) that since chlorins are characterized by an intense absorption in the red, the material which he called isoporphin might actually be a chlorin, i.e., a porphyrin in which one of the pyrrole nuclei is reduced. Calvin, Ball and Aranoff were able to show (3,p.2259) that an oxidation-reduction relationship existed between the two materials in the case of  $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin

(Figure 1).

In a later, more complete study Ball, Dorough, and Calvin (1,p.2278) were able to show by three independent chemical methods and also by analysis that the two main products of the reaction of benzaldehyde and pyrrole are  $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin and , , , -tetraphenylchlorin.

When N-methylporphyrins became available, Corwin and Erdman carried out a spectroscopic study (8,p.1885) in an attempt to determine whether hydrogen bonding exists in porphyrins. The visible spectra of the acid, basic, and copper complex salts of etioporphyrin II (Figure 1) were obtained and compared with those of N-methyletioporphyrin II and the etioporphyrin II free base. While the spectra of the salts are quite similar, that of the free base is drastically different indicating a very different bond distribution. The tagging of one nitrogen by a methyl group destroys the possibility of N-equivalence. On the supposition of hydrogen bonding in the molecule this should produce a drastic change in the spectrum, according to Erdman and Corwin. However, if the hydrogens are uniquely placed, substitution of a methyl group for a hydrogen should produce only a slight perturbation. The spectrum of N-methyletioporphyrin II compared to that of the unsubstituted porphyrin shows only



a rather uniform shift to the red averaging about 20 millimicrons. Erdman and Corwin conclude that if hydrogen bonding does exist it does not occur to an extent which appreciably alters the electronic energy of the molecule.

In an attempt to clarify the situation regarding hydrogen bonding in porphyrin, Vestling and Downing (25, p.3511) studied the infrared spectra of 3,4',5-trimethyl-3',4-dicarbethoxy-5'-bromodipyrromethene, etioporphyrin I, and their copper complex salts in the hydrogen stretching region. Peaks at 3.03 microns ( $3301\text{ cm.}^{-1}$ ) in the case of the dipyrromethene and 3.01 microns ( $3321\text{ cm.}^{-1}$ ) in the case of the porphyrin were identified as NH stretches by virtue of their disappearance in the copper salts. Since the absorption peaks differ from the pyrrole NH peak at 2.94 microns ( $3400\text{ cm.}^{-1}$ ) hydrogen bonding is indicated. Vestling and Downing point out that infrared spectroscopy can give evidence for intramolecular bonding only when a set of absorption frequencies can be compared with those exhibited by like acceptors and donors in different molecules, a method which is inapplicable in this case. Thus it must be admitted that the shift in the NH frequency may be due only to a change in the character of the pyrrole nucleus in the formation of the compounds.

The fact that N-isomers of the type postulated by Rothmund have never been isolated may be attributed to

one of two reasons according to Dorrough and Shen (7,p.3939). Either the energy required for tautomerism is too small to permit a physical separation of the two isomers or else the hydrogen atoms are bonded in some entirely different manner which precludes the possibility of NH isomerism at all. One such structure would be an ionic one (Figure 2, 3). Another is a hydrogen bonded one (Figure 2, 5 and 6). Dorrough and Shen reject these structures for the following reason. Both structures contain imino nitrogens with abnormally bonded hydrogens. However, Corwin and Erdman's work on the visible spectra of etioporphyrin II and N-methyletioporphyrin II indicates that the hydrogens are bonded in a normal manner. It was proposed to detect the existence of possible NH isomers by comparing spectroscopic measurements in the visible region made at room temperature with those made at liquid nitrogen or liquid air temperatures. The lowering of the temperature should shift the equilibrium to favor the more stable tautomer and if the spectra of the two tautomers differ enough, then the spectrum at low temperatures should differ from the supposedly composite room temperature spectrum. Such a change was actually found, with the low temperature spectrum showing shifts and evidence of unresolved fine structure. Fluorescence spectra were also obtained at low temperatures. When the exciting light was in different

regions of the fine structure, different fluorescence spectra were produced. Dorrough and Shen interpret these results as supporting the proposition that porphin free bases exist as equilibrium mixtures of compounds resulting from the tautomerism of the imino hydrogens. They also suggest that the position of the NH stretching absorption in etioporphyrin I observed by Vestling and Downing may be due to the contribution of resonance forms such as (4) in Figure 2.

## THE ANALYSIS OF INFRARED SPECTRA

## NORMAL COORDINATES

Absorption in the infrared region of the spectrum is assigned to molecular vibration and rotation. In classical terms, an infrared active vibration or rotation produces a variation in the dipole moment of the molecule which occurs with the frequency of the motion. This variation allows the molecule to interact with an electromagnetic field in such a manner as to absorb energy. In those molecules having no dipole moment and where vibration does not produce a dipole moment no interaction can take place and no absorption occurs.

The determination of molecular structure by means of infrared spectroscopy is essentially a trial and error process. Ordinarily a reasonable structure is assumed and the spectrum predicted on this basis. The degree of success in correlating the predicted and observed spectra is taken to be a measure of the accuracy of the assumed model.

The prediction of the spectrum is made fundamentally from the selection rules (12, pp. 251-271; 2, pp. 82-94). However all pertinent information, such as the form of the vibrations, probable values of force constants, etc., is utilized as far as possible. The selection rules,



obtained from quantum mechanics and group theory, focus attention on the symmetry of the potential function of the absorbing unit. For the gas phase this symmetry is described by the point group of the molecule. Selection rules for the crystalline state have been discussed by Halford (11, pp. 8-15) and by Hornig (13, pp. 1063-1076). In this case the environment of the molecule in the crystal must be considered, i.e., the site group or the cell group. The determination of the site group or the cell group requires a knowledge of the crystal structure, specifically the space group of the crystal.

It will be useful at this point to discuss briefly the meaning of normal coordinates (2, pp. 66-71; 12, pp. 61-82; 4, pp. 122-126) and the origin of the selection rules. The configuration of the molecule may be expressed in Cartesian displacement coordinates, i.e., a coordinate system in which the equilibrium position of each atom in the molecule is made the origin of a 3-dimensional Cartesian coordinate system. In this coordinate system the kinetic energy is given by

$$2T = \sum_{i=1}^N m_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2)$$

or

$$2T = \sum_{i=1}^{3N} m_i \dot{x}_i^2$$

where the coordinates have simply been relabeled.

The potential energy of the system may be expanded in a Taylor series about the origin

$$\begin{aligned} V = V_{eq} &+ \sum_{i=1}^{3N} \left( \frac{\partial V}{\partial x_i} \right) x_i = 0 x_i \\ &+ \sum_{i,j=1}^{3N} \left( \frac{\partial^2 V}{\partial x_i \partial x_j} \right) x_i x_j = 0 x_i x_j \\ &+ \sum_{i,j,k=1}^{3N} \left( \frac{\partial^3 V}{\partial x_i \partial x_j \partial x_k} \right) x_i x_j x_k = 0 x_i x_j x_k \\ &+ \dots \end{aligned}$$

$V_{eq}$ , the potential energy at the equilibrium position, is an arbitrary additive constant and may be set equal to zero. Since

$$x_1 = x_j = x_k = \dots x_{3N} = 0$$

is by definition an equilibrium position

$$\left( \frac{\partial V}{\partial x_i} \right)_{x_i=0} = 0 \quad i = 1, 2, 3, \dots, 3N.$$

For sufficiently small displacements the cubic and higher terms may be neglected so that  $V$  becomes



$$V = \sum_i \sum_j f_{ij} x_i x_j$$

where

$$f_{ij} = \left( \frac{\partial^2 V}{\partial x_i \partial x_j} \right)_{x_i, x_j = 0}.$$

If a transformation to mass-weighted coordinates  $q$ , where

$$q_i = \frac{x_i}{\sqrt{m_i}}$$

is now made, the kinetic and potential energies become

$$2T = \sum_i^{3N} \dot{q}_i^2$$

$$2V = \sum_{i,j}^{3N} f_{ij} q_i q_j$$

where

$$f_{ij} = \frac{f_{ij}'}{\sqrt{m_i m_j}}.$$

It may be shown that there exists a transformation

$$Q_i = \sum_j A_{ij} q_j$$

which brings the kinetic and potential energies into the form

$$2T = \sum_{i=1}^{3N} \dot{Q}_i^2$$

$$2V = \sum_{i=1}^{3N} \lambda_k Q_k^2$$

The  $Q$ 's are known as the normal coordinates. It will be seen that the wave equation becomes separable in the normal coordinates, which allows the molecule to be considered as a collection of independent oscillators.

In terms of the normal coordinates Lagrange's equations become

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{Q}_i} \right) - \frac{\partial L}{\partial Q_i} = 0$$

$$\frac{d}{dt} (\dot{Q}_i) + \lambda_k Q_k = 0$$

$$\ddot{Q}_k + \lambda_k Q_k = 0$$

$$Q_k = Q_{0k} \cos (\omega t + \sigma)$$

The form of the equations indicates that the normal coordinate  $Q_k$  corresponds to one of the vibrational modes of the system, provided  $\lambda_k$  is positive. The normal coordinates corresponding to zero or negative values of  $\lambda_k$  are non-periodic and represent translation and rotation of the molecule.

Suppose only one normal coordinate  $Q_1$  is different from zero. Then since

$$q = \underline{A}^{-1} Q$$

or

$$q_i = \sum_j A^{-1}_{ij} Q_j$$

it may be seen that this describes a situation in which all the atoms move with the same frequency in such a way that the Cartesian components of the displacements change according to sine curves. This is characteristic of normal vibrations.

The normal coordinates are unique in that they allow the kinetic and potential energies to be expressed as the sums of squares. Any conceivable vibrational motion of the molecule may be represented by a superposition of the normal coordinates with the proper phase and amplitude. Since it may be shown that  $Q$ 's are orthogonal, the transformation

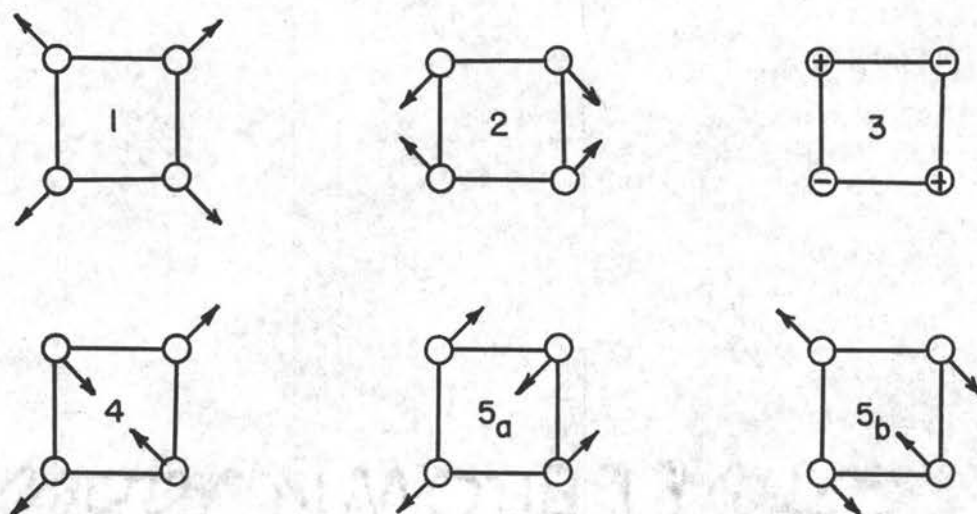
$$Q = \underline{A} q$$

is simply a rotation of the mass-weighted coordinate system.

Consideration of how the normal coordinates transform under the symmetry operations appropriate to the

molecule leads to their classification into symmetry types or species (2,p.71; 12,pp.82-131; 4,pp.143-153). This may be conveniently discussed in terms of a hypothetical square, planar, tetratomic molecule. For such a molecule the normal vibrations are as indicated in Figure 3a.

FIGURE 3a  
NORMAL VIBRATIONS OF A  $D_{4h}$  MOLECULE



The symmetry or covering operations of a molecule are those operations (rotations or rotations followed by reflections) which leave it in a configuration



indistinguishable from the original configuration. For the molecule under discussion they are the identity operation (I), rotation of  $90^\circ$  either way about an axis perpendicular to the plane of the molecule and passing through the center of gravity ( $2C_4$ ), a rotation of  $180^\circ$  about the same axis ( $C_2$ ), a rotation of  $180^\circ$  about an axis in the plane of the molecule and passing through opposite sides ( $2C_2'$ ), rotation of  $180^\circ$  about an axis in the plane of the molecule and passing through opposite corners ( $2C_2''$ ), reflection in the plane of the molecule ( $\sigma_h$ ), a rotation of  $90^\circ$  about an axis perpendicular to the plane of the molecule followed by reflection in the plane of the molecule ( $S_4$ ), rotation of  $180^\circ$  about the same axis followed by reflection in the plane of the molecule (i), reflection in a plane perpendicular to the plane of the molecule and passing through the centers of opposite sides ( $\sigma_v$ ), and reflection in a similar plane passing through opposite corners ( $\sigma_d$ ). These operations form a group in the mathematical sense.

The behavior of the normal coordinates under the symmetry operations may be represented in the following way (taking  $Q_2$ ,  $Q_{5a}$ , and  $Q_{5b}$  as examples).

		$\chi(Q)$
$IQ_2 = Q_2$	$[1]$	1
$C_4Q_2 = -Q_2$	$[-1]$	-1
$C_2Q_2 = Q_2$	$[1]$	1
$C_2'Q_2 = -Q_2$	$[-1]$	-1
$C_2''Q_2 = -Q_2$	$[-1]$	-1
$\sigma_hQ_2 = Q_2$	$[1]$	1
$S_4Q_2 = -Q_2$	$[-1]$	-1
$IQ_2 = Q_2$	$[1]$	1
$\sigma_dQ_2 = -Q_2$	$[-1]$	-1
$\sigma_vQ_2 = Q_2$	$[1]$	1

.....

$IQ_{5a} = Q_{5a}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	2
$IQ_{5b} = Q_{5b}$		
$C_4Q_{5a} = Q_{5b}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	0
$C_4Q_{5b} = Q_{5a}$		
$C_2Q_{5a} = -Q_{5a}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	-2
$C_2Q_{5b} = -Q_{5b}$		
$C_2'Q_{5a} = -Q_{5b}$	$\begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$	0
$C_2'Q_{5b} = -Q_{5a}$		
$C_2''Q_{5a} = Q_{5a}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	0
$C_2''Q_{5b} = -Q_{5b}$		



		$\chi(Q)$
$\sigma_h Q_{5a} = Q_{5a}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	2
$\sigma_h Q_{5b} = Q_{5b}$		
$S_4 Q_{5a} = -Q_{5b}$	$\begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$	0
$S_4 Q_{5b} = -Q_{5a}$		
$I Q_{5a} = -Q_{5a}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	-2
$I Q_{5b} = -Q_{5b}$		
$\sigma_v Q_{5a} = -Q_{5b}$	$\begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$	0
$\sigma_v Q_{5b} = -Q_{5a}$		
$\sigma_d Q_{5a} = Q_{5a}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	0
$\sigma_d Q_{5b} = -Q_{5b}$		

Thus for a given non-degenerate  $Q$  or pair of doubly degenerate  $Q$ 's a transformation matrix may be associated with each group operation. Since a one-to-one correspondence exists between the symmetry operators and the transformation matrices and since the matrices obey the group postulates in the same way as the symmetry operators, the matrices form an (irreducible) representation of the symmetry point group. Each set of matrices corresponds to a possible kind of behavior under the symmetry operations, i.e., a symmetry type or species. Other considerations lead to the conclusion that there are ten symmetry species

in the case of the point group  $D_{4h}$ . These are given in the character table for the group, which is obtainable from purely group theoretical considerations. It gives the characters (the sum of the diagonal elements) of the transformation matrices. Since this quantity is the same for symmetry operators of a given class (such as the two  $C_4$ 's) and since it is an invariant it constitutes sufficient identification. The character table for the point group  $D_{4h}$  is given in Table 1, page 26. A given row is to be associated with a possible type of behavior of a normal coordinate under the symmetry operations.

If degenerate vibrations are present it is necessary to have some knowledge of the potential function in order to obtain the normal coordinates. In the absence of such knowledge, however, it is always possible to obtain symmetry coordinates (12, pp. 145-148; 2, pp. 77-80). These are coordinates which have the proper transformation properties for the symmetry species under consideration. The normal coordinates are linear combinations of the symmetry coordinates, the coefficients depending on the force constants.

#### SELECTION RULES FOR GASES

According to quantum mechanics, the appearance of a line resulting from a transition from a vibrational state of quantum number  $v_1$  to one of quantum number  $v_2$

TABLE 1

CALCULATION OF NORMAL MODES AND  
ACTIVITIES OF A  $D_{4h}$  MOLECULE

$D_{4h}$	I	$2C_4$	$C_2''$	$2C_2$	$2C_2'$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$	$2S_4$	1	n	
$A_{1g}$	1	1	1	1	1	1	1	1	1	1	1	
$A_{1u}$	1	1	1	1	1	-1	-1	-1	-1	-1	0	
$A_{2g}$	1	1	1	-1	-1	1	-1	-1	1	1	0	
$A_{2u}$	1	1	1	-1	-1	-1	1	1	-1	-1	0	IR
$B_{1g}$	1	-1	1	1	-1	1	1	-1	-1	1	1	
$B_{1u}$	1	-1	1	1	-1	-1	-1	1	1	-1	1	
$B_{2g}$	1	-1	1	-1	1	1	-1	1	-1	1	1	
$B_{2u}$	1	-1	1	-1	1	-1	1	-1	1	-1	0	
$E_g$	2	0	-2	0	0	-2	0	0	0	2	0	
$E_u$	2	0	-2	0	0	2	0	0	0	-2	1	IR
	0	$\pi/4$	$\pi/2$	$\pi/2$	$\pi/2$	0	0	0	$\pi/4$	$\pi/2$	$\phi$	
	2	0	-2	-2	-2	2	2	2	0	-2	$2 \cos \phi$	
	3	1	-1	-1	-1	1	1	1	-1	-3	$\pm 1 + 2 \cos \phi$	
	4	0	0	0	2	4	0	2	0	0	$U_R$	
	6	-2	2	2	0	4	0	2	0	0	$(U_R - 2) \chi(M)_R$	
											or $U_R \chi(M)_R$	

depends (2,p.85) on the quantity

$$\int \chi_{v_1}^*(Q) M \chi_{v_2}(Q) d\tau$$

This integral must be invariant under the symmetry group of the molecule. For fundamentals

$$v_2 - v_1 = 1,$$

and if some symmetry operation changes the sign of  $Q$  then the integral will change sign (and thus vanish) unless  $M$  changes sign also. If the integral is to be non-vanishing, then  $M$  must have the same character as  $Q$ . Thus the problem is to find which linear combinations, if any, of the components of the dipole moment have the same character as the coordinates of a given species. This is equivalent to determining how many times a given irreducible representation (corresponding to one of the normal coordinates) occurs in the reducible representation defined by the dipole moment. The character in the representation defined by the components of the dipole moment is

$$\pm 1 + 2 \cos \phi$$

since the components of a vector transform like Cartesian coordinates.



If the quantity

$$\frac{1}{N} \sum h_p (\pm 1 + 2 \cos \phi) \chi_j(R)$$

vanishes (2,p.89) no combination of  $M_x$ ,  $M_y$ ,  $M_z$  transforms like the normal coordinate in question so that absorption cannot occur. Here  $N$  is the order of the group,  $h_p$  is the number of operations in a class,  $\chi_j(R)$  is the character of species  $R$  under operation  $j$  and the summation is taken over all the classes in the group. If the summation does not vanish the mode will be infrared active only when

$$\frac{\partial M}{\partial Q} \neq 0.$$

These methods permit the classification of the normal coordinates into symmetry and the determination of the activity of the species.

The preceding discussion assumes a knowledge of the normal coordinates. However such knowledge is not necessary for the following reason. It is simple to obtain a reducible Cartesian representation of the symmetry group for a given molecule. Formulas from group theory may then be applied to determine how many times a given irreducible representation is contained in the reducible Cartesian representation and thus how many normal modes of vibration of the molecule belong to a given symmetry species.

The reducible Cartesian representation may be obtained as follows, taking the operation  $C_4$  as an example. This operation takes the displacement of atom 1, rotates it  $90^\circ$  and transfers it to atom 2, the displacement of atom 2 is rotated and transferred to atom 3, etc. This transformation must be represented (4,p.145) by a matrix of the form

$$\begin{bmatrix} 0 & 0 & 0 & S \\ S & 0 & 0 & 0 \\ 0 & S & 0 & 0 \\ 0 & 0 & S & 0 \end{bmatrix}$$

where  $S$  is a submatrix of the form

$$\begin{bmatrix} \cos \pi/4 & \sin \pi/4 & 0 \\ -\sin \pi/4 & \cos \pi/4 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The quantity of interest is the character of the reducible representation. The various matrices need not be written to obtain this for it is seen that only atoms which are not moved will contribute to the character and these will contribute

$$\begin{aligned} 2 \cos \phi \pm 1 & \quad + 1 \text{ pure rotations} \\ & \quad - 1 \text{ rotation-reflections.} \end{aligned}$$

The character for a given operation in the reducible representation is then

$$\chi = U_R (2 \cos \phi \pm 1)$$

where  $U_R$  is the number of atoms whose position is unchanged by the operation. To eliminate the contributions made to the character by translations and rotations this must be modified to

$$\chi = (U_R - 2)(1 + 2 \cos \phi) \quad \text{rotation}$$

or

$$\chi = U_R (-1 + 2 \cos \phi) \quad \text{rotation-reflection}$$

The number of normal vibrations in a given symmetry species is given by

$$n = \frac{1}{N} \sum_R h_R \chi_R \cdot \chi_R (R)$$

where  $\chi_R$  is the character of the reducible representation and the other symbols have their previous meanings.

The use of these methods may be illustrated by their application to the square, planar, tetratomic molecule discussed in the preceding section. The calculations necessary to determine the number of vibrations belonging to a given symmetry species and the infrared activity of the species are rather simple as will be evident from the following.

The character table for the point group  $D_{4h}$  is given in Table 1, along with the activity of the various species and the number of vibrations in each species for

the molecule in question. Comparison of the transformation matrices obtained in the preceding section with the character table shows that  $Q_2$  belongs to species  $B_{1g}$  while  $Q_{5a}$  and  $Q_{5b}$  belong to the degenerate species  $E_u$ . Similar considerations would show that  $Q_1$  is  $A_{1g}$ ,  $Q_3$  is  $B_{1g}$ , and  $Q_4$  is  $B_{2g}$ .

It is seen that the only infrared active vibration is the degenerate one  $Q_5$ . While vibrations of  $A_{2u}$  symmetry are also active no vibrations of this species is possible for the molecule.

As an example of the calculations involved, consider the species  $B_{1g}$ . The number of vibrational coordinates belonging to this species is given by

$$n(B_{1g}) = \frac{1}{16} \left[ (1)(1)(6) + (2)(-1)(-2) + (1)(1)(2) \right. \\ + (2)(1)(2) + (2)(-1)(0) + (1)(1)(4) \\ + (2)(1)(0) + (2)(-1)(2) + (2)(-1)(0) \\ \left. + (2)(-1)(0) \right] \\ n(B_{1g}) = 1$$

Thus there is one vibration of species  $B_{1g}$ , namely  $Q_3$ . The infrared activity is determined by the value of the summation

$$\frac{1}{16} \left[ (1)(1)(3) + (2)(-1)(1) + (1)(1)(-1) + (2)(1)(-1) \right. \\ + (2)(-1)(-1) + (1)(1)(1) + (2)(1)(1) + (2)(-1)(1) \\ \left. + (2)(-1)(-1) + (1)(1)(-3) \right]$$



Since the summation vanishes the species  $B_{1g}$  is inactive in the infrared.

#### ANHARMONICITY

The previous discussion has been based on the assumption that the cubic and higher terms in the expression for the potential energy may be neglected. If the molecule is sufficiently rigid, the vibrational displacements are small compared to the internuclear distances and the approximation is somewhat justified. However the presence of anharmonic terms gives rise to important effects (12, pp. 201-221; 19, pp. 211-216) and these will be discussed here.

In diatomic molecules the presence of anharmonicity is made obvious by the fact that such molecules may dissociate. The potential energy must approach a constant value with increasing internuclear distances. In classical terms, this flattening of the potential curve indicates a dependence of frequency on amplitude.

The motion of an anharmonic oscillator, while periodic in time, must be described by a Fourier series rather than a single sine or cosine term. This series will contain, in addition to a term whose frequency is that of the motion, terms whose frequencies are multiples of this. In classical radiation theory, absorption and emission of radiation is closely connected with this

Fourier series. The presence of the higher terms in the series indicates that multiples of the fundamental frequency, or harmonics, will be present in the spectrum.

In polyatomic molecules there is, in addition to the appearance of harmonics and the dependence of frequency on amplitude, coupling between the various normal modes. In the presence of this coupling the resolution of the motion into normal modes is no longer clear-cut. The excitation of one normal mode results eventually in the transfer of energy to other modes. The frequency of a normal vibration depends not only on its own amplitude but on the amplitude of the other vibrations as well. Sums and differences of two or more normal vibrations, called combinations, may appear.

Usually these effects are small but if the frequency of one normal vibration happens to be nearly one-half the frequency of another normal vibration or if the sum of two frequencies nearly equals a third, resonance effects may occur. These resonance effects greatly enhance the effects due to anharmonicity.

These same results appear in the quantum theory. Corresponding to a decrease in frequency with increasing amplitude there is a decrease in the separation of vibrational levels with increasing energy. Corresponding to harmonics and overtones are transitions between other

than neighboring levels. If the vibrational levels were equidistant the transitional frequency between second neighbors would be just twice that between adjacent levels. Actually the spacing is not uniform so that while this transition between second neighbors corresponds to the second harmonic, its frequency is not exactly twice that of the first harmonic as in classical theory.

In polyatomic molecules simultaneous changes of quantum numbers of more than one normal vibration may occur. This gives rise to the appearance of sum and difference frequencies. In quantum theory as well as classical theory these combination tones and overtones have low intensities compared to the intensities of the fundamentals. If the molecule has symmetry, selection rules based on this symmetry come into play and not all of the combinations and overtones may be allowed.

#### SELECTION RULES FOR CRYSTALS

For molecules in the crystalline phase consideration must be given to the environment. In crystals where intermolecular forces are weak the vibrations of the molecule may be expected to be little affected (19, pp. 216-220).

The rotation of the molecule will almost always be strongly influenced. Except for cases of so-called free rotation the rotation is actually transformed into a

vibration about a fixed equilibrium position. The translation of the molecule is likewise transformed into a vibration. Thus in solids all degrees of freedom may be considered to be vibrational.

With the change of rotation into vibration the pure rotational spectrum is replaced by frequencies corresponding to a faster oscillatory motion. At the same time the rotational structure of the internal molecular vibration is effectively eliminated. This structure contained sums and differences of vibrational and rotational frequencies. Instead of this structure we now have combination tones between internal vibrations which have replaced rotation in the crystal. But, as usual, these combination tones have low intensities compared to the fundamentals, so that the strongest absorptions correspond to simple vibrations. The disappearance of rotational structure gives rise to a narrowing of the absorption region belonging to the vibrations. This narrowing is often overcompensated by effects due to coupling of internal vibrations.

The influence of neighboring molecules also affects the intensities of the transitions. If a symmetrical molecule is placed in unsymmetrical surroundings, the symmetry reasons for the absence of a frequency from the infrared spectrum may no longer be valid. Thus vibrations



appear which are forbidden in the gaseous state.

Halford (11, pp.8-15) treats the motions of the molecule in a potential field reflecting the symmetry of the surrounding crystal. This permits the use of point symmetry rather than space symmetry and yields a suitable number of frequencies with appropriate selection rules. While this is an idealization it has the virtue of simplicity and has basis in the fact that intermolecular coupling may be small in the crystal.

The use of this approach requires a knowledge of the crystal structure. Attention is focussed on points in the crystal structure called sites. These sites lie on one or more symmetry elements and the operations of the space group generate a number of equivalent sites which is less than the order of the group. It is a well known rule of crystallography that the centers of gravity of symmetrical molecules are located on sites and thus the potential energy has the symmetry of the site. The occupant of a site is taken as an example of the symmetry of the motions of a molecule and these motions are assigned to symmetry species without regard to the motions of the rest of the crystal. This assignment is made with the reservation that the molecular motions are coupled to some extent. The relation between the motions of an isolated molecule and those of one in the crystal may be

established by comparison of the molecular group and the site group.

Since the site group must be a subgroup of the space group and the molecular group, comparison of these eliminates all but a few symmetries. Halford gives a list (11, pp. 14-15) of the site groups contained in each space group.

Hornig discusses (13, pp. 1063-1073) the selection rules on the basis of the unit cell group. This group is obtained from the space group by considering the translations of the space group to be equivalent to the identity. Emphasis is placed on giving the selection rules a rigorous basis in symmetry.

It is shown that in the harmonic oscillator approximation only a very small number of modes may be active. These modes are totally symmetric with respect to translation, and have the proper symmetry with respect to the unit cell group. Calculations made on the basis of the site group are shown to give results identical to those obtained with the use of the unit cell group.

In the harmonic approximation the spectrum should consist of very sharp lines and the wide lines obtained experimentally are attributed to coupling between molecular and lattice modes as a result of anharmonicity.

## CHARACTERISTIC FREQUENCIES

Since the normal modes of vibration of given molecule are unique, there is no particular reason to expect similarities in the spectra of different compounds. It is a matter of experimental observation (18, pp. 1-18), however, that compounds of similar structure have similar spectra and that the presence of a certain structural feature results in the presence of one or two bands in the infrared spectrum.

Consider, for example, compounds containing the  $\equiv\text{C-H}$  bond. Such compounds invariably exhibit absorption bands in the vicinity of  $3000\text{ cm.}^{-1}$  and  $700\text{ cm.}^{-1}$ . The theories of valence indicate that the binding of the hydrogen should be nearly the same in all of these compounds. Since the mass of the hydrogen atom is much smaller than that of the rest of the molecule its amplitude in a normal vibration will be comparatively much larger. Since the hydrogen atom is an end atom it can only move in the line of the bond or perpendicular to it. That is, it can execute only stretching and bending vibrations. If, as a first approximation, the hydrogen is considered to vibrate against an infinite mass the stretching and bending will depend only on the bending and stretching force constants. Since the force constants are dependent on the bonding, these compounds would be

expected to exhibit two characteristic frequencies, one corresponding to CH stretching and the other to CH bending. These have been assigned to the frequencies  $3000\text{ cm.}^{-1}$  and  $700\text{ cm.}^{-1}$  respectively.

#### SELECTION RULES FOR PORPHIN

The calculations of the preceding sections require some initial assumptions. For molecules in the gaseous phase this assumption is in the form of a symmetry point group for the molecule. For molecules in the crystalline phase it is necessary to know the space group of the crystal. While the main features of the structure of the porphin molecule have been well established by the methods of organic chemistry, the bonding of the imino hydrogens is still open to question. In addition, no information on the crystal structure of porphin is available, although some work has been done on the related tetraphenylporphin and tetraphenylmonazaporphin (27, pp. 601-603). These compounds were found to belong to the same space group,  $C_{2h}^5(P2_1/a)$ , as the phthalocyanines but the unit cell dimensions differ considerably. Considerable alteration in the intensities of reflections was also observed. These changes could not be accounted for without assuming a considerable change in the packing of the molecules.

This ambiguity concerning the structure of porphin is not a serious handicap for the following reasons. Since



the molecule is relatively large, changes in the position or bonding of the imino hydrogens would be expected to have only a minor effect on the selection rules. The results of work with phthalocyanine (14,p.94) and naphthalene (16,pp.270-277) indicate that for large covalent molecules, selection rules based on the molecular point group rather than the site or cell group are adequate. The work with these compounds indicates that the coupling of vibrations in the crystal will make itself evident in the weak splitting of degeneracies, weak appearance of combination bands, etc. This is not surprising, in that for crystals of such compounds, intramolecular forces are expected to be of much more importance than intermolecular ones. Thus the molecular point group can be employed with some confidence.

If it is assumed that the imino hydrogens are placed at equal distances above and below the center of the plane of the molecule, the symmetry is  $D_{4h}$ . This assumption is almost certainly not correct but is justified for the reason already mentioned. In the metalloporphin, with the hydrogens no longer present, the assumption of  $D_{4h}$  symmetry seems to be a straightforward one. If the possible elongation of the molecule, found in phthalocyanine, is taken into account the same assumption about the imino hydrogens gives  $D_{2h}$  symmetry; while

again the metalloporphin is obviously also  $D_{2h}$ . The calculations made on the basis of these assumed symmetries are given in Tables 2 and 3, pages 42 and 43.

It is seen that for porphin with  $D_{4h}$  symmetry, only 24 absorptions are predicted although the molecule has 108 vibrational degrees of freedom. This speaks for the high symmetry of the assumed model.

The vibrations may be analyzed in terms of internal coordinates to provide additional information. Decius has given a method (6, pp. 1315-1318) for defining such coordinates of the stretching, bending, out-of-plane bending, and torsional types. This method gives a kinematically complete set of vibrational coordinates with no redundancies in acyclic molecules and with  $6\mu$  redundancies in cyclic molecules, where  $\mu$  is the number of bonds which must be cut to render the molecule acyclic.

These coordinates may be used to obtain a representation of the symmetry group in much the same way as was indicated for the normal coordinates. This representation may be employed as before to classify linear combinations of the internal coordinates into symmetry species. In general the actual form of the normal vibrations cannot be obtained but an indication of what kinds of motions, in terms of bond stretches, torsions, etc., which go to make them up is given. This information is useful because

TABLE 2

CALCULATION OF NORMAL MODES  
FOR PORPHIN AND COPPER PORPHIN OF  $D_{4h}$  SYMMETRY

											n		
$D_{4h}$	I	$2C_4$	$C_2''$	$2C_2$	$2C_2'$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$	$2S_4$			H <sub>2</sub>	Cu
A <sub>1g</sub>	1	1	1	1	1	1	1	1	1	1	1	10	9
A <sub>2g</sub>	1	1	1	-1	-1	1	-1	-1	1	1	1	8	8
B <sub>1g</sub>	1	-1	1	1	-1	1	1	-1	-1	1	1	9	9
B <sub>2g</sub>	1	-1	1	-1	1	1	-1	1	-1	1	1	9	9
E <sub>g</sub>	2	0	-2	0	0	-2	0	0	0	2	2	9	8
A <sub>1u</sub>	1	1	1	1	1	-1	-1	-1	-1	-1	-1	3	3
A <sub>2u</sub>	1	1	1	-1	-1	-1	1	1	-1	-1	-1	6	6
B <sub>1u</sub>	1	-1	1	1	-1	-1	-1	1	1	-1	-1	5	5
B <sub>2u</sub>	1	-1	1	-1	1	-1	1	-1	1	-1	-1	4	4
E <sub>u</sub>	2	0	-2	0	0	2	0	0	0	-2	-2	18	18
	37	1	1	3	5	37	3	5	1	1	1	U <sub>R</sub> (Cu)	
	38	2	2	2	4	36	4	6	0	0	0	U <sub>R</sub> (H <sub>2</sub> )	
	3	1	-1	-1	-1	1	1	1	-1	-3	-3	$\pm 1 + 2 \cos \phi$	

n number of vibrational modes  
Cu copper porphin  
H<sub>2</sub> porphin  
IR infrared active

TABLE 3

CALCULATION OF NORMAL MODES  
FOR PORPHIN AND COPPER PORPHIN OF  $D_{2h}$  SYMMETRY

									n		
$D_{2h}$	I	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	1	$C_2(z)$	$C_2(y)$	$C_2(x)$	$H_2$	Cu	
$A_g$	1	1	1	1	1	1	1	1	19	18	
$B_{1g}$	1	1	-1	-1	1	1	-1	-1	17	17	
$B_{2g}$	1	-1	1	-1	1	-1	1	-1	9	8	
$B_{3g}$	1	-1	-1	1	1	-1	-1	1	9	8	
$A_u$	1	-1	-1	-1	-1	1	1	1	8	8	
$B_{1u}$	1	-1	1	1	-1	1	-1	-1	10	10	IR
$B_{2u}$	1	1	-1	1	-1	-1	1	-1	18	18	IR
$B_{3u}$	1	1	1	-1	-1	-1	-1	1	18	18	IR
	3	1	1	1	-3	-1	-1	-1	$\pm 1 + 2 \cos \phi \chi(M)_R$		
	38	36	4	4	0	2	2	2	$U_R(H_2)$		
	37	37	3	3	1	1	3	3	$U_R(Cu)$		

n    number of vibrational modes  
 $H_2$     porphin  
Cu    copper porphin  
IR    infrared active



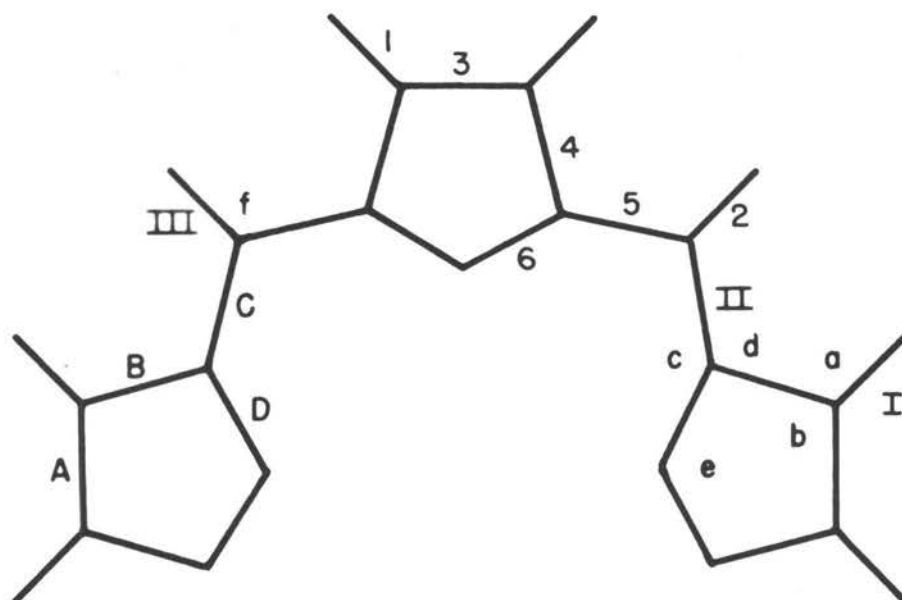
characteristic frequencies are usually given in terms of such stretches or torsions.

This approach focuses attention on the symmetry of the bond system of the molecule rather than the equilibrium positions of the nuclei. If the bonds to the imino hydrogens are considered, the molecule no longer has  $D_{4h}$  or even  $D_{2h}$  symmetry. For this reason they will be ignored in the treatment of the internal coordinates. The definition of the remaining internal coordinates is given in Figure 4, page 45.

The character corresponding to a given bond type and symmetry operation is given by

$$\chi(\alpha)_R = \begin{array}{l} \text{number of coordinates of type} \\ \alpha \text{ unshifted by operation } R \end{array}$$

That this is the character is evident from the consideration that only those coordinates which are unshifted will result in the appearance of an element on the diagonal of the associated matrix. When a diagonal element does appear its value will be 1. If the coordinate is shifted into its negative, the character will of course be negative. The character thus obtained is used in the same way as before to obtain the number of linear combinations of a given coordinate in a particular symmetry species. The results of the calculation are given in Table 4.



Bond	Stretches	
1	CH (1)	8
2	(2)	4
3	CC (1)	4
4	(2)	8
5	(3)	8
6	CN	<u>8</u>
		40

Bending (inplane)		
a	CCH (1)	8
b	CCC (1)	8
c	NCC	8
d	CCC (2)	8
e	CNC	4
f	CCH (2)	<u>8</u>
		44

Torsions		
A	HCCH	4
B	HCCC (1)	8
C	(2)	8
D	CCNC	<u>8</u>
		28

Bending (out of plane)		
I	CH (1)	8
II	CC	8
III	CH (2)	<u>4</u>
		20

DEFINITION OF INTERNAL COORDINATES  
FOR PORPHIN - H<sub>2</sub>

FIGURE 4

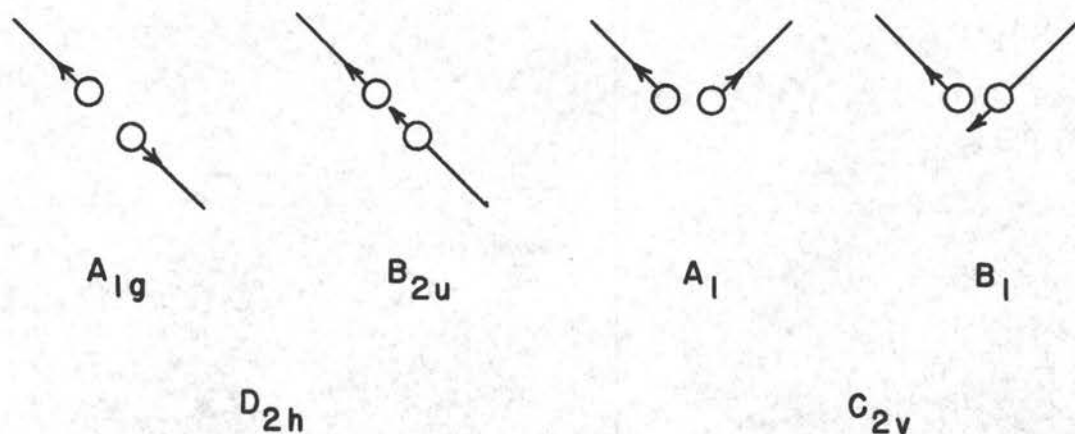
TABLE 4

## SYMMETRY PROPERTIES OF INTERNAL COORDINATES IN PORPHIN

	1	2	3	4	5	6	a	b	c	d	e	f	A	B	C	D	I	II	III	Total Modes	Mol. Modes
A <sub>1g</sub>	1	1	1	1	1	1	1	1	1	1	1	1	0	0	0	0	0	0	0	12	9
A <sub>2g</sub>	1	0	0	1	1	1	1	1	1	1	0	1	0	0	0	0	0	0	0	9	8
B <sub>1g</sub>	1	0	1	1	1	1	1	1	1	1	1	1	0	0	0	0	0	0	0	11	9
B <sub>2g</sub>	1	1	0	1	1	1	1	1	1	1	0	1	0	0	0	0	0	0	0	10	9
E <sub>1g</sub>	0	0	0	0	0	0	0	0	0	0	0	0	1	2	2	2	2	2	1	12	8
A <sub>1u</sub>	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	0	6	3
A <sub>2u</sub>	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	6	5
B <sub>1u</sub>	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	7	5
B <sub>2u</sub>	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	0	5	4
E <sub>1u</sub>	2	1	1	2	2	2	2	2	2	2	1	2	0	0	0	0	0	0	0	21	17

The contribution of the imino hydrogens to the spectrum may be discussed on the basis of a simplified model in which it is assumed that the NH bonds lie in the plane of the molecule and that the mass of the remainder of the molecule is infinite. If the hydrogens are assumed to be bonded to opposite nitrogens the symmetry is  $D_{2h}$  while the assumption that they are bonded to adjacent nitrogens gives  $C_{2v}$  symmetry. If only the stretching motions are considered two modes of vibration are expected. For the  $D_{2h}$  model one of these is  $A_{1g}$  and inactive while the other is  $B_{2u}$  and active. For the  $C_{2v}$  model the modes are  $A_1$  and  $B_1$ , both of which are active.

FIGURE 3b  
VIBRATIONS OF THE IMINO HYDROGENS



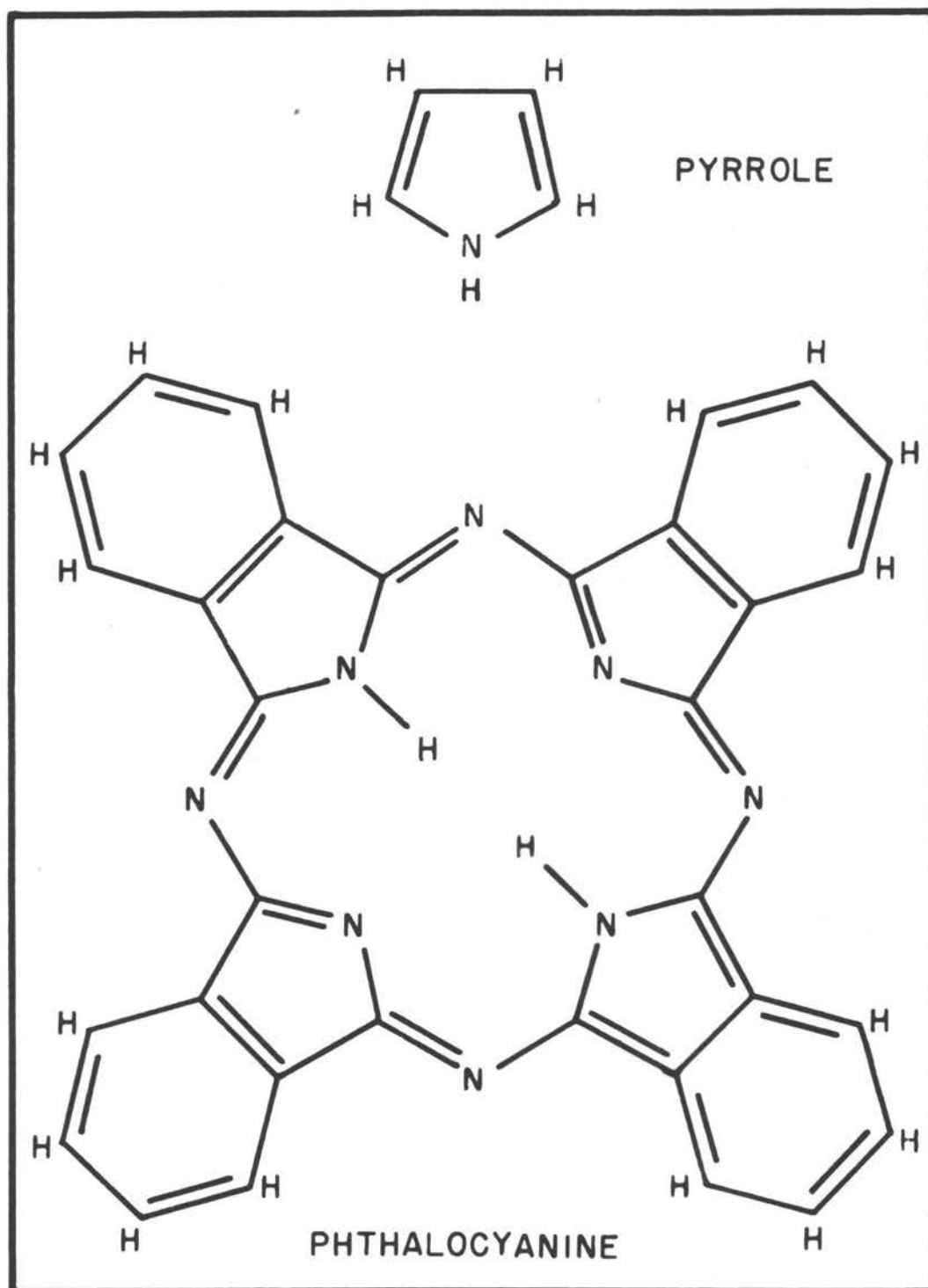


Thus if the imino hydrogens are bonded to opposite nitrogens only one NH stretching frequency is expected, while if they are bonded to adjacent nitrogens or if the compound is a mixture of the two forms more than one should be obtained. The application of this criterion depends, of course, on the ability to resolve two frequencies if they are present. They would be expected to lie rather close together.

#### THE INFRARED SPECTRA OF PHTHALOCYANINE AND PYRROLE

The use of the method of characteristic frequencies requires a knowledge of the spectra of similar compounds. Similarity of structure implies similarity in spectra. If careful study has led to the assignment of frequencies, these assignments may often be transferred. This procedure must be used with due allowance for unsuspected structural effects.

The resemblance between the porphyrins and the phthalocyanines is evident from a comparison of Figure 1 and Figure 5. In the porphyrins the benzene rings of the phthalocyanine are missing and the nitrogens which link the four similar nuclei have been replaced by methyldyne (methenyl groups). The porphyrins contain four pyrrole nuclei (Figure 5). Two of these have retained the N-hydrogen, while the other two have lost it. In addition they have combined through the methyldyne linkages in



STRUCTURAL FORMULAS FOR  
PHTHALOCYANINE AND PYRROLE

FIGURE 5

such a way as to form an eighteen-membered conjugated ring. The two hydrogen-retaining nuclei participate in this ring formation in a different way than do those which have lost the hydrogen.

In view of the preceding discussion it is expected that there will be a correspondence between the spectra of, on the one hand porphin, and on the other pyrrole and phthalocyanine. Fortunately both of these molecules have been studied intensively, pyrrole by Lord and Miller (15, pp.328-341) and phthalocyanine by Karasek (14, pp.1-120).

Lord and Miller studied pyrrole, pyrrole-N-d, symmetrical pyrrole-d<sub>4</sub>, and pyrrole-d<sub>5</sub>. Both the Raman and infrared spectra were obtained, the latter in the liquid state for the region 750-1900 cm.<sup>-1</sup>. The use of the deuterated compounds allowed a rather complete assignment of the frequencies. These assignments are given in Table 6.

Karasek obtained the spectra of phthalocyanine, phthalocyanine-N-d<sub>2</sub>, and the copper, nickel, platinum, and magnesium phthalocyanines in the region 400-3500 cm.<sup>-1</sup>. The compounds were studied in the form of sublimed films. The assignments for the absorptions are given in Table 5.

TABLE 5  
ASSIGNMENTS FOR PHTHALOCYANINE

<u>Frequency (cm.<sup>-1</sup>)</u>	<u>Assignment</u>
3290	NH stretch
3078	
3043	
3026	benzene CH stretch
3013	
1616	benzene CC stretch
1507	inner ring CN stretch
1475	benzene CC stretch
1442	inner ring CN stretch
1340	benzene CC stretch (CCH bend)
1285	inner ring CN stretch
1194	CC stretch (ortho carbons)
1163	inner ring CN stretch
1123	CCH parallel bend
1098	CCH parallel bend
1010	NH IP bend
946	CH perp.
872	
886	CH perp.



TABLE 5 (Cont'd.)

<u>Frequency (cm.<sup>-1</sup>)</u>	<u>Assignment</u>
777	CH perp.
767	
736	CN inner ring perp.
715	CH perp.
684	CCC parallel bend
616	
556	CN inner ring
492	
443	CCC benzene ring

TABLE 6  
ASSIGNMENTS FOR PYRROLE

	<u>Frequency</u> <u>(cm.<sup>-1</sup>)</u>	<u>C<sub>2v</sub></u> <u>Symmetry</u>	<u>Assignment</u>
v <sub>9</sub>	3400	A <sub>1</sub>	NH stretch
v <sub>8</sub>	3133	A <sub>1</sub>	CH stretch (s)
v <sub>17</sub>	(3133)	B <sub>1</sub>	CH stretch (a)
v <sub>16</sub>	3111	B <sub>1</sub>	CH stretch (a)
v <sub>7</sub>	3100	A <sub>1</sub>	CH stretch (a)
v <sub>15</sub>	1530	B <sub>1</sub>	ring stretch (a)
v <sub>6</sub>	1467	A <sub>1</sub>	ring stretch (s)
v <sub>14</sub>	1418	B <sub>1</sub>	ring stretch (a)
v <sub>5</sub>	1384*	A <sub>1</sub>	ring stretch (s)
v <sub>4</sub>	1237	A <sub>1</sub>	CH IP bend
v <sub>3</sub>	1144	A <sub>1</sub>	ring stretch (breathing)
v <sub>13</sub>	(1146)	B <sub>1</sub>	NH IP bend
v <sub>2</sub>	1076	A <sub>1</sub>	CH IP bend (s)
v <sub>12</sub>	1046	B <sub>1</sub>	CH IP bend (a)
v <sub>24</sub>	(1046)	B <sub>2</sub>	CH OP bend
v <sub>11</sub>	1015	B <sub>1</sub>	CH IP bend
v <sub>20</sub>	868	A <sub>2</sub>	CH OP bend
v <sub>23</sub>	838	B <sub>2</sub>	CH OP bend

TABLE 6 (Cont'd.)

	<u>Frequency</u> (cm. <sup>-1</sup> )	<u>C<sub>2v</sub></u> <u>Symmetry</u>	<u>Assignment</u>
v <sub>1</sub>	711	A <sub>1</sub>	ring bending (s)
v <sub>19</sub>	(711)	A <sub>2</sub>	OP ring bend
v <sub>22</sub>	768	B <sub>2</sub>	NH and CH OP bend
v <sub>10</sub>	647	B <sub>1</sub>	ring bend (a)
v <sub>18</sub>	[510]	A <sub>2</sub>	OP ring bend
v <sub>21</sub>	565	B <sub>2</sub>	NH OP bend

a = antisymmetric

s = symmetric

IP = inplane

OP = out of plane

() = used twice

[ ] = calculated with prod. rule

\* = IR freq. value, R band diffuse

## EXPERIMENTAL

## PREPARATION OF MATERIALS

Pyrrolealdehyde. The pyrrolealdehyde was prepared by the method of Fischer (26,p.403). The aldehyde was used as obtained from the vacuum distillation, no recrystallization being performed.

Porphin. The porphin was prepared by the method of Fischer and Gleim (9,pp.157-160), however, the isolation and purification was done chromat graphically rather than by means of acid fractionation.

Two hundred grams of 100% formic acid (Baker's Analyzed) was placed in a three-necked, 250 ml., round-bottomed flask, fitted with a stirrer and reflux condenser and placed in an oil bath. With the formic acid refluxing, 20 grams of pyrrolealdehyde dissolved in 40 ml. of absolute alcohol was introduced into the flask by means of a Hershberg dropping funnel. The flow was regulated so that the addition took place over a period of 24 hours. Heating was continued for an additional 12 hours or until the reaction mixture became so viscous as to prevent stirring. The mixture was then transferred to a 1-liter beaker and neutralized with concentrated ammonia, filtered, and the residue washed thoroughly with cold water. The residue was then dried in a desiccator over calcium chloride. The



dried material, after being ground with a mortar and pestle, was extracted for several hours in a Soxhlet apparatus with about 125 ml. of pyridine (Baker's Analyzed). The pyridine extract was poured into 600 ml. of peroxide-free ether. The ether solution was then washed with four or five 100 ml. portions of water, filtered, and evaporated to dryness. The residue was taken up in chloroform (ACS grade) and chromatographed on alumina. The column used was tightly packed and measured 3x25 cm. A sharp separation was obtained, much dark-colored material remaining at the top of the column and the porphin appearing as a rose-red band. This band was eluted with more chloroform.

The chloroform solutions from a number of such runs were combined, concentrated and rechromatographed. A small amount of dark-colored material was separated from the product in this way. The porphin was obtained by evaporating the chloroform solution to dryness. It was then recrystallized once from pyridine-methanol. Since the compound has no melting point the only means of checking its purity consists of measuring its visible absorption spectrum. However, the sharpness of the chromatographic separation combined with the good agreement of its visible spectrum with that given by Fischer and Gleim (9,p.158) leave little room for doubt on this

score.

Copper Porphin (21,p.627). Ten milligrams of porphin was taken up in 20 ml. of boiling glacial acetic acid. The boiling solution was removed momentarily from the hot plate and 100 mg. of copper acetate,  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , and 300 mg. of sodium acetate  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$  added. The mixture was replaced on the hot plate and boiled for an additional two minutes. The solution was then transferred into 500 ml. of ether using 50 ml. of water, and the ether layer washed with several portions of water. The ether layer was filtered and dried over sodium sulfate. The copper salt was obtained by evaporation of this solution to dryness. The visible spectrum of the ether solution was in good agreement with that given by Rothmund.

#### SAMPLE PREPARATION

The infrared spectra of solids are commonly obtained with the material in the form of a mull in some suitable liquid. This method suffers from several disadvantages. If the material is very hard it may be difficult to reduce the particle size in the mull to a point where scattering losses are low. In addition, the liquid medium has absorptions of its own. These absorptions may obscure those due to the sample itself. While it is true that this may be corrected for to some extent

by running a blank, accurate data become difficult to obtain. Although these difficulties are not insurmountable it was thought to be more expedient to employ methods in which they are not encountered. Two such methods are those in which use is made of sublimed films and pressed potassium bromide windows.

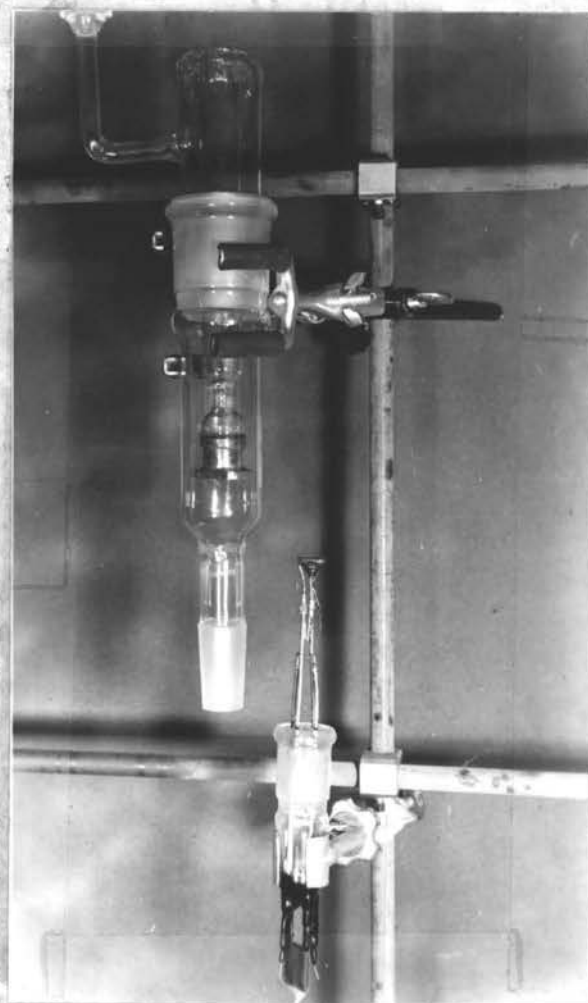
Sublimed Films. These films are produced by placing a heated sample of material close to a relatively cool window of some suitable material (14,p.58; 23,p.299). The sample vaporizes and then deposits on the window, a process probably more accurately described as molecular distillation. In the most favorable cases a tightly adhering film with low scattering losses is produced. The thickness of the film may be controlled by regulating the time allowed for the deposition. Karasek's success (14,p.60) with sublimed films of phthalocyanines suggested the use of this method for porphin. Preliminary trials indicated that the apparatus employed by Karasek to produce films of phthalocyanines would be ineffective for porphin. Another factor was the relative instability to heat of porphin.

To overcome these difficulties a sublimation unit was constructed in which the aims were to provide minimum separation of sample and window, effective cooling of the window, and good control of the temperature of the sample.

The unit which evolved is pictured in Plate 1, page 60. To prepare a film, a window of suitable material is attached to the copper block on the cold finger, the sample placed on the heater, and the unit assembled and attached to a high-vacuum manifold. After pumping down to about  $10^{-5}$  mm., the refrigerant (dry ice-acetone or liquid nitrogen) is introduced into the cold finger and heat applied to the sample. The temperature, as indicated by the copper-constantan thermocouple attached to the plate on which the sample rests, is controlled by adjustment of the Variac which supplies the heater wire. With moderately close attention the temperature can be held within an interval of about  $20^{\circ}$ . The heating is maintained until a film of the desired thickness is obtained, the cold finger being kept supplied with refrigerant. Then the voltage applied to the heater is removed and the refrigerant allowed to evaporate. After allowing the window to come to room temperature, to avoid the condensation of water, the manifold is brought up to atmospheric pressure and the sublimator removed and disassembled to obtain the window.

Pressed Potassium Bromide Windows. The use of pressed KBr windows is a relatively recent technique (24, pp.1805-1808). In this method the sample is ground in a mortar, being mixed thoroughly with powdered potassium





THE SUBLIMATION APPARATUS

PLATE 1

bromide. The sample-KBr mixture is then placed in the assembled die and ring, the plunger put into place, and the plunger-die-ring assembly then inserted in the outer chamber. The chamber is pumped out and finally the whole assembly placed in a hydraulic press. A pressure of about twenty tons is then applied, the chamber is opened, and the finished disc is pushed out. If properly done, the disc will be transparent and free from cracks or translucent spots.

The quality of the disc depends rather critically on the potassium bromide. Scraps of single crystals grown from the melt<sup>2</sup> have been used successfully. These are powdered in an agate or mullite mortar and used without further treatment. The amount of potassium bromide used is in the range of 200-400 mg. with sample concentrations of 0.06 to 2.0 %.

#### SPECTRA

The Spectrometer. The spectrometer used for the measurements to be described here has been described in detail elsewhere (14, pp.32-50). It is based on a Perkin-Elmer 12C monochromator. This has been modified by the Halford-Savitsky method to make possible the automatic

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<sup>2</sup> Obtainable from the Harshaw Chemical Co., Elyria, Ohio.

recording of the spectra. The radiation from the source is modulated or "chopped" so that the output from the detecting element, a thermocouple, is a pulsating direct current whose magnitude depends on the amount of the radiation reaching it. This output is amplified by a high gain amplifier tuned to the modulation frequency. The amplified signal is rectified by means of a phase-discriminating breaker, filtered, and applied to a recording potentiometer. As the rotation of the prism causes the wavelength of the radiation reaching the thermocouple to sweep through the spectrum the potentiometer produces a record of transmitted energy versus wavelength. Point by point division of the curve obtained with the sample by that obtained with the blank gives the percentage transmission of the sample versus wavelength. This procedure is known as the single beam method.

In the double beam method both sample and blank are placed in the beam. In this case the chopping disc used is cut so that the modulation of the sample and blank beams is  $90^{\circ}$  out of phase. The breaker system following the amplifier discriminates between the two components of the amplified signal and provides two DC voltages, one proportional to the amount of radiation passing through the blank, and the other to that passing through the sample. The output from the blank is applied to the

slidewire of the potentiometer and the sample output is applied to the potentiometer itself. The balancing action of the potentiometer then provides a direct plot of the percentage transmission of the sample versus wavelength.

The prism of the monochromator may be changed to take advantage of the dispersive properties of the various prisms available. These include lithium fluoride, sodium chloride, and potassium bromide.

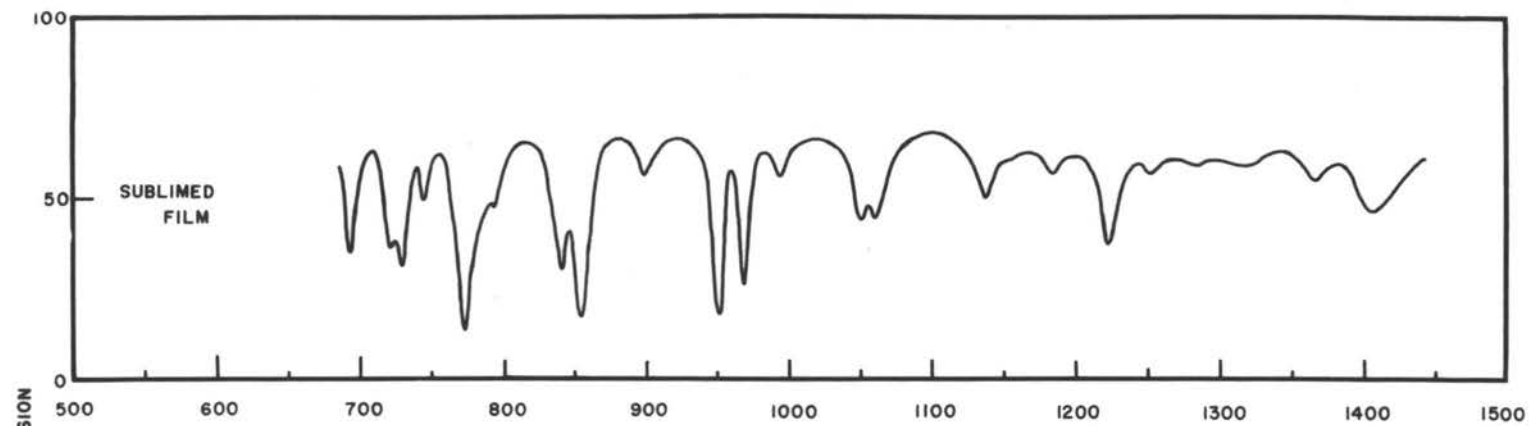
Sublimed Films. Attempts to prepare sublimed films of porphin met with disappointing results as there seemed to be a definite limit to the thickness of the film which could be produced. Under these circumstances it is difficult to determine whether weak bands are being missed. The film whose spectrum is given in Figure 6, page 64, was produced by repeated sublimation, the window being replaced in the sublimer after its spectrum had been recorded and the sublimation procedure repeated. The total time of sublimation for this film was 6-1/2 hours at a temperature of about  $300^{\circ}$  and a pressure of less than  $10^{-5}$  mm. using liquid nitrogen as a refrigerant.

Etioporphyrin II<sup>3</sup> was found to sublime much more readily than porphin. The film whose spectrum is given in

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<sup>3</sup> Contributed by Mr. Richard M. Teeter of the Department of Chemistry and Chemical Engineering of the University of Washington.





THE INFRARED ABSORPTION OF PORPHIN  
500 - 1500  $\text{cm}^{-1}$

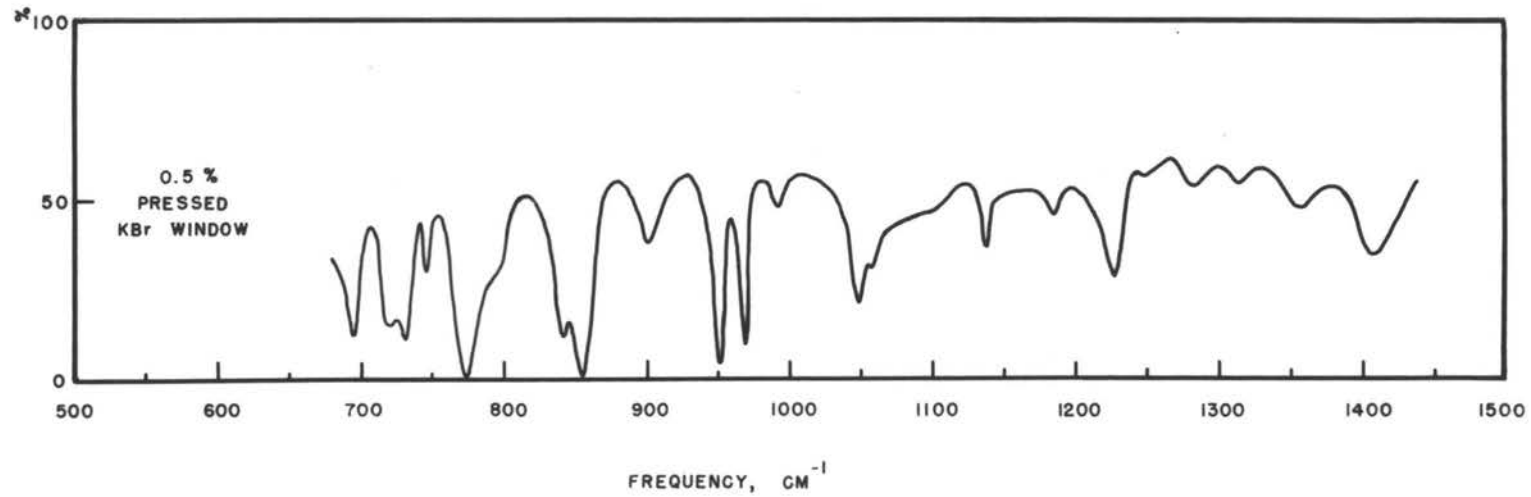


FIGURE 6

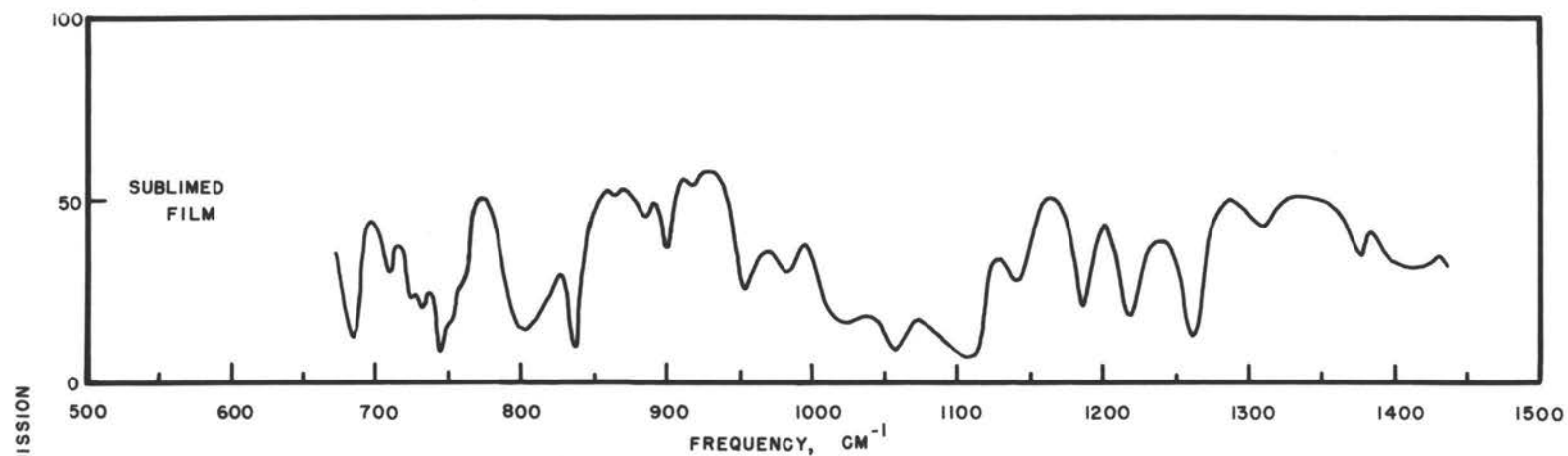
Figure 7, page 66, was produced in 1 hour at a pressure of  $10^{-5}$  mm. using dry ice-acetone as a refrigerant. The temperature, though not measured, was probably not more than  $150^{\circ}$ .

Attempts to produce a sublimed film of copper porphin under conditions similar to those used with porphin met with complete failure.

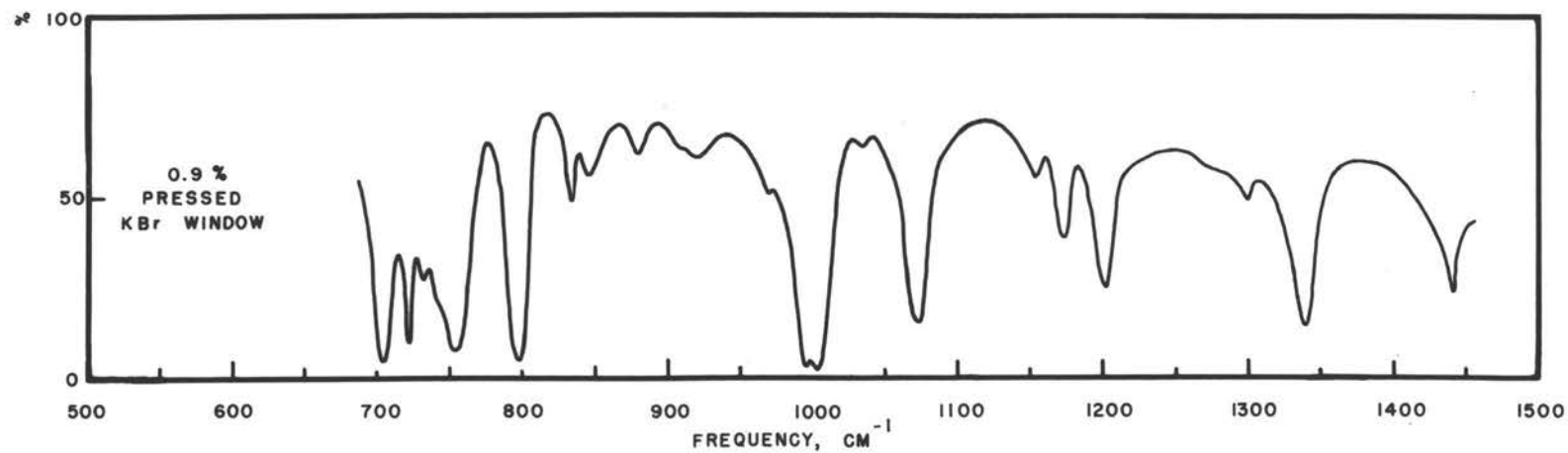
Pressed Windows. The window press was employed to produce samples of porphin, copper porphin, and zinc tetraphenylporphin<sup>3</sup>. The potassium bromide used was cut from single crystals<sup>2</sup>. Total weight of the windows was about 300 mg. The press used was a Carver laboratory press, a pressure of 12,000 psi being maintained for ten minutes. The outer chamber was evacuated with a Cenco Hyvac pump for a few minutes before pressure was applied and the pumping was continued during the pressing. The spectra of the samples are given in Figures 6, 7, 8 and 9.

The curves in Figure 9, unlike those in the other figures, are not percentage transmission plots. The high dispersion of the lithium fluoride prism used in this region gives a slowly decreasing background so that a direct plot of the potentiometer reading versus frequency provides sufficient information.

It is seen that the bands, for the most part, are quite sharp. The spectra of the porphin sublimed film



THE INFRARED ABSORPTION OF ETIOPORPHYRIN II  
500-1500 CM<sup>-1</sup>



THE INFRARED ABSORPTION OF ZINC TETRAPHENYLPORPHIN  
500-1500 CM<sup>-1</sup>

FIGURE 7

and pressed window are in good agreement except in the region  $2700\text{--}2800\text{ cm.}^{-1}$ . This point will be discussed later. The spectrum of the copper salt, in addition to other changes, shows an extremely strong, broad absorption in the region  $1050\text{--}1150\text{ cm.}^{-1}$ . No such broad absorption appears in the zinc tetraphenylporphin spectrum which is more similar in character to those of the free bases than to that of the other metal salt.

In an attempt to determine whether the absorption in the  $1050\text{--}1150\text{ cm.}^{-1}$  region for the copper porphin was due to an impurity the 1.0% window was powdered, placed in a bomb, sealed to a high-vacuum line and baked out at  $150^\circ$  and  $10^{-5}$  mm. for 12 hours. During this treatment a light orange film, apparently consisting of copper porphin which had sublimed out of the mixture, appeared on the cooler glass surface above the heating path. After removal from the bomb, the powder was repressed. The window obtained in this way showed no change in the character of the  $1050\text{--}1150\text{ cm.}^{-1}$  region, other than a slight decrease in intensity which is probably due to the decrease in the strength of the sample as a result of the sublimation.

Low Temperature Measurements. Dorrough and Shen's observation (7, pp.3939-3944) of a change in the visible spectrum of tetraphenylporphin on going from room



temperature to liquid nitrogen temperature suggested a similar experiment in the infrared region. It was also of interest to determine the effect of lowering the temperature on the strong, broad band in copper porphin.

The cell used for these measurements is of a type common for low temperature infrared work. It consists essentially of a Dewar vessel provided with a sample holder at the end of the inner vessel and sodium chloride windows for the passage of the infrared energy. The 0.5% porphin window, sandwiched between silver chloride plates to provide for good heat conduction, was placed in the cell. After evacuating the cell to  $10^{-5}$  mm. the spectrum of the window was recorded single beam with the sodium chloride prism. Liquid nitrogen was then introduced into the cold finger and the spectrum recorded again. After an hour's cooling with liquid nitrogen, no change in the spectrum other than a slight narrowing and shifting of the bands, was observed. The same treatment was given to the 0.5% copper porphin window with special attention to the  $1050-1150 \text{ cm.}^{-1}$  region. No pronounced effects were observed although there was a slight narrowing and shifting of the absorption.

The frequencies of the bands observed in the various porphyrins are given in Tables 7 and 8.

TABLE 7

ABSORPTION BANDS OBSERVED FOR PORPHYRINS  
IN THE REGION 500-1600  $\text{cm}^{-1}$

<u>Porphin</u>	<u>Copper Porphin</u>	<u>Etio- porphyrin II</u>	<u>Zinc Tetra- phenylporphin</u>
650	580	684	703
694	648	709	722
720	700	723	732
731	745	732	743?
746	770	744	754
773	778	751?	798
795	799	760?	833
841	833?	803	846
855	857	817?	880
900	880	836	910?
951	950	863vw	920
969	963	885	970vw
992	993	898	995
1048	1020	918vw	1004
1057	1062	953	1034vw
1100?	1119	983	1073
1137	1135?	1023	1153
1185	1218	1057	1173
1227	1295?	1108	1202
1248	1400	1139	1277?
1282		1187	1300
1315		1218	1340
1357		1261	1440
1407		1311	
		1378	
		1412	

TABLE 8

ABSORPTION BANDS OBSERVED FOR PORPHYRINS  
IN THE REGION 2750-3600  $\text{cm}^{-1}$

<u>Porphin</u>		<u>Copper Porphin</u>	<u>Etiopor- phyrin II</u>	<u>Zinc Tetra- phenylporphin</u>
<u>Sublimed Film</u>	<u>Pressed Window</u>			
2852m	2852w	2832?vw	2862s	2850?vw
2925m	2930w	2857?vw	2928s	2930w
3040w	3041w	2896?vw	2965s	2996w
3107m	3108m	2930w	3065w	3029m
3315m	3312m	3045?(sh)	3322s	3054m
	3430m	3105m		3100w
		3440m		3122w
				3431m

m      medium  
w      weak  
vw     very weak  
s      strong  
sh     shoulder  
?      uncertain because of weakness  
         or unresolved

ASSIGNMENTS  
FOR THE REGION 500-1500  $\text{cm}^{-1}$

Pyrrole exhibits several absorptions below 700  $\text{cm}^{-1}$  which have been assigned to out of plane ring bending and NH out of plane bending. The failure to observe all of these bands, or ones closely related to them, in the compounds under discussion here is probably due to a combination of low sample concentrations and low background transmission. The 580  $\text{cm}^{-1}$  band in the copper porphin is doubtless due to an out of plane pyrrole ring bending. The 650  $\text{cm}^{-1}$  band observed in both porphin and its copper salt may be readily associated with an inplane pyrrole ring bending which occurs at 647  $\text{cm}^{-1}$ .

Absorption bands appear in porphin (P) at 694  $\text{cm}^{-1}$  and in etioporphyrin II (EP) at 684  $\text{cm}^{-1}$ . If the bands in copper porphin (C) at 700  $\text{cm}^{-1}$  and zinc tetraphenylporphin (ZTP) at 704  $\text{cm}^{-1}$  are not grouped with this pair it may be assigned to NH out of plane bending. The frequency assigned to this motion in pyrrole is 565  $\text{cm}^{-1}$ . A shift in this frequency in going from pyrrole to porphin is expected. Whether it would be this large is difficult to state.

If the 722  $\text{cm}^{-1}$  band in zinc tetraphenylporphin is assigned to phenyl CH out of plane bending (715  $\text{cm}^{-1}$  in phthalocyanine), the remaining bands in this region



may be grouped in pairs. In porphin the bands of the pair 720, 731  $\text{cm}^{-1}$  are about equally intense. The same is true for the etioporphyrin II 723, 732  $\text{cm}^{-1}$  pair. In zinc tetraphenylporphin the higher component, 732  $\text{cm}^{-1}$  is distinctly weaker than the lower 704  $\text{cm}^{-1}$ . The copper porphin band at 700  $\text{cm}^{-1}$  has no higher companion unless it is the band at 745  $\text{cm}^{-1}$ . Absorption bands in pyrrole at 711  $\text{cm}^{-1}$  and in furan at 725  $\text{cm}^{-1}$  have been assigned to in-plane ring bending. This suggests the assignment of these pairs to in-plane bending of nonequivalent pyrrole nuclei. There is also the possibility that they represent the splitting of a  $D_{4h}$   $E_u$  mode into the  $B_{2u}$  and  $B_{3u}$  modes of  $D_{2h}$ .

Bands appear at 746  $\text{cm}^{-1}$  (P), 745  $\text{cm}^{-1}$  (C), 744  $\text{cm}^{-1}$  (EP), while zinc tetraphenylporphin displays a shoulder at about 743  $\text{cm}^{-1}$ . These bands are assigned to an in-plane C-C-C bending, the reduced intensity in the zinc salt suggesting that it may involve principally the methylidyne carbons.

The bands appearing at 773  $\text{cm}^{-1}$  (P) and 770  $\text{cm}^{-1}$  (C) are assigned to pyrrole CH out of plane bending. An absorption appearing at 768  $\text{cm}^{-1}$  in pyrrole was assigned to CH and NH out of plane bending. The relatively high intensity of the band in the copper salt suggests that in pyrrole the motion is principally CH bending. Shoulders

appear in the etioporphyrin II at  $751\text{ cm.}^{-1}$  and  $760\text{ cm.}^{-1}$  but these may be assigned to methyl out of plane bending. A strong absorption occurs in zinc tetraphenylporphin at  $754\text{ cm.}^{-1}$ , a rather larger shift than occurs for the copper salt. However this absorption may be alternatively assigned to a twisting in the phenyl groups if it is assumed that the CH bending is much reduced in intensity but not shifted.

A band at  $795\text{ cm.}^{-1}$  is resolved in the porphin sublimed film but appears as a shoulder in the pressed windows. Etioporphyrin II has a stronger broader absorption at  $803\text{ cm.}^{-1}$ , while copper porphin and zinc tetraphenylporphin have bands at  $799\text{ cm.}^{-1}$  and  $798\text{ cm.}^{-1}$  respectively. This is not a pyrrole frequency unless it is much shifted. It is assigned to C-C-C in-plane bending possibly involving the methylidyne carbon.

The bands appearing at  $841\text{ cm.}^{-1}$  (P),  $836\text{ cm.}^{-1}$  (EP), the shoulder at  $833\text{ cm.}^{-1}$  (C) and one of the pair  $833, 846\text{ cm.}^{-1}$  (ZTP) are readily associated with the  $838\text{ cm.}^{-1}$  band in pyrrole and are thus assigned to out of plane pyrrole ring bending. The other member of the  $833, 846\text{ cm.}^{-1}$  (ZTP) pair is then assigned to phenyl CH bending.

The bands appearing at  $855\text{ cm.}^{-1}$  (P),  $857\text{ cm.}^{-1}$  (C),  $863\text{ cm.}^{-1}$  (EP), and  $846\text{ cm.}^{-1}$  (ZTP) may be assigned to an in-plane C-C-C bending. While the etioporphyrin II

band is much weaker than the others of this group this may be a result of the presence of the methyl and ethyl groups. A pyrrole band at  $868\text{ cm.}^{-1}$  was assigned to CH out of plane bending by Lord and Miller. However this motion has the  $C_{2v}$  symmetry  $A_2$  and would go into the  $A_{1u}$  or  $B_{2u}$  species of  $D_{4h}$ . These species are inactive in the infrared.

Bands appear at  $900\text{ cm.}^{-1}$  (P),  $898\text{ cm.}^{-1}$  (EP),  $880\text{ cm.}^{-1}$  (ZTP) and a shoulder at about  $880\text{ cm.}^{-1}$  (C). Pyrrole has no absorptions in this region but an absorption in pyridine at  $884\text{ cm.}^{-1}$  has been assigned to C-C-C perpendicular bending. Following this lead these bands are assigned to a similar motion in the porphyrins. The lower frequency of the zinc tetraphenylporphin band suggests the possibility that this motion involves the methyldiyne carbons.

The bands occurring at  $951\text{ cm.}^{-1}$  (P),  $953\text{ cm.}^{-1}$  (EP) and  $950\text{ cm.}^{-1}$  (C) have no counterpart in the spectrum of the zinc tetraphenylporphin. The assignment of an absorption at  $940\text{ cm.}^{-1}$  in pyridine to CH out of plane bending suggests the assignment of these bands to methyldiyne CH out of plane bending. This would explain the absence of this band in the zinc salt.

The bands at  $969\text{ cm.}^{-1}$  (P),  $963\text{ cm.}^{-1}$  (C),  $970\text{ cm.}^{-1}$  (ZTP) and  $983\text{ cm.}^{-1}$  (EP) have no counterpart in

pyrrole. They may be assigned to C-C stretching in the porphyrin nucleus. The same assignment is made for the bands  $992\text{ cm}^{-1}$  (P),  $993\text{ cm}^{-1}$  (C), and one of the pair  $995, 1004\text{ cm}^{-1}$  (ZTP). The other member of the zinc tetraphenylporphin is then assigned to phenyl CC stretching. Possibly the very weak etioporphyrin II  $983\text{ cm}^{-1}$  band is also to be associated with this group. If the stretching involves the beta carbons in the pyrrole nuclei the presence of methyl and ethyl groups on these carbons in etioporphyrin II would be expected to reduce the amplitude of the vibration and thus also the intensity of the absorption.

The pairs of bands  $1048, 1057\text{ cm}^{-1}$  (P),  $1020, 1062\text{ cm}^{-1}$  (C) and  $1034, 1074\text{ cm}^{-1}$  (ZTP) may be associated with the pair of CH in-plane bends appearing at  $1046\text{ cm}^{-1}$  and  $1076\text{ cm}^{-1}$  in pyrrole. The bands at  $1023\text{ cm}^{-1}$  and  $1057\text{ cm}^{-1}$  in etioporphyrin II are then assigned to motions of the methyl and ethyl groups.

Bands appearing at  $1137\text{ cm}^{-1}$  (P),  $1139\text{ cm}^{-1}$  (EP),  $1119\text{ cm}^{-1}$ ,  $1135\text{ cm}^{-1}$  (C) and  $1153\text{ cm}^{-1}$  (ZTP) have a counterpart in the pyrrole spectrum at  $1146\text{ cm}^{-1}$ . Lord and Miller assign this band to a pyrrole ring stretch with an alternative assignment to NH in-plane bending. It is difficult to choose between these alternatives for the porphyrins. The copper porphin bands are different in



character from the bands in the other compounds, being much stronger and broader. If the motion involved is a pyrrole CN stretch the shifting, broadening and splitting may be attributed to the result of the nitrogens being bonded to copper. Qualitatively the same effect would be expected for the zinc salt but here the shift is in the opposite direction, and the band is neither particularly broadened or strengthened. Thus one may assign the  $1137\text{ cm}^{-1}$  (P) and  $1139\text{ cm}^{-1}$  (EP) bands to NH in-plane bending and attempt to make alternative assignments for the bands in the salts. Possibly the bands in copper porphin are connected to a motion of the metal atom, and that in the zinc salt to a vibration of the phenyl groups.

Bands appear at  $1185\text{ cm}^{-1}$  (P),  $1187\text{ cm}^{-1}$  (EP) and  $1173\text{ cm}^{-1}$  (ZTP). The broad, strong absorption of the copper porphin in this region renders a decision difficult but certainly no strong band is present. Furan has an absorption at  $1189\text{ cm}^{-1}$  which is assigned to ring stretching. If this assignment is transferred the absence of a stronger or sharper band in the copper salt may be attributed to an anchoring of the nitrogens by the copper. This supposes that the motion is principally an in-plane C-N-C bending. Alternatively the  $1153\text{ cm}^{-1}$  zinc tetraphenylporphin band may be associated with this group and the  $1173\text{ cm}^{-1}$  band assigned to phenyl C-C

stretching.

The assignment of the pyrrole  $1237\text{ cm}^{-1}$  band to in-plane CH bending suggests that a similar assignment be made for  $1227\text{ cm}^{-1}$  (P) and  $1218\text{ cm}^{-1}$  (C). However this would not explain the appearance of a band in etioporphyrin II at  $1218\text{ cm}^{-1}$ . Thus it seems more likely that these bands are due to a methyldyne CH in-plane bending. The  $1202\text{ cm}^{-1}$  band in the zinc salt is then assigned to phenyl C-C stretching.

The weakness of the bands at  $1248\text{ cm}^{-1}$ ,  $1282\text{ cm}^{-1}$  and  $1315\text{ cm}^{-1}$  in porphin together with a lack of correlation between the various spectra suggests that they are combination bands. However the groups  $1357\text{ cm}^{-1}$  (P),  $1378\text{ cm}^{-1}$  (EP),  $1340\text{ cm}^{-1}$  (ZTP) and  $1407\text{ cm}^{-1}$  (P),  $1412\text{ cm}^{-1}$  (EP) and  $1440\text{ cm}^{-1}$  (ZTP) may be assigned to pyrrole ring in-plane stretching.

ASSIGNMENTS  
FOR THE REGION 2750-3600  $\text{cm}^{-1}$

Since hydrogen bonding is almost certainly present in porphin the NH stretching frequency may be expected to appear somewhat below the frequency  $3400 \text{ cm}^{-1}$  assigned to it in pyrrole and nearer the phthalocyanine value,  $3290 \text{ cm}^{-1}$ . The band at  $3312 \text{ cm}^{-1}$  in porphin and the one at  $3322 \text{ cm}^{-1}$  in etioporphyrin II are in the correct range and since no corresponding bands appear in either of the metal salts they are assigned to NH stretching. This is also in accord with Vestling and Downing's assignment (25, p.3513) of a band at  $3320 \text{ cm}^{-1}$  in a solution of etioporphyrin I to this motion.

The fact that a single, relatively narrow band appears is significant in regard to the question of the bonding of the imino hydrogens, since it agrees with the assumption of approximately  $D_{2h}$  symmetry. This supports the belief that the hydrogens are bonded to opposite hydrogens. The relative sharpness of the band argues against the existence of more than one absorption. It is possible however, that while two nitrogen isomers may exist in solution the crystal structure of porphin favors the existence of the  $D_{2h}$ -like molecule.

Pyrrole exhibits bands at  $3105 \text{ cm}^{-1}$  and  $3135 \text{ cm}^{-1}$ , the  $3105 \text{ cm}^{-1}$  band being a doublet. Lord and Miller

assign these bands to CH stretching, namely two  $A_1$ ,  $B_1$  pairs involving both the alpha and beta hydrogens. The bands at  $3108\text{ cm.}^{-1}$  (P),  $3105\text{ cm.}^{-1}$  (C), and the pair  $3100\text{--}3122\text{ cm.}^{-1}$  (ZTP) are readily assigned to pyrrole CH stretching in the corresponding porphyrins. However no bands corresponding to the  $3135\text{ cm.}^{-1}$  pyrrole frequency appear in the porphyrins with the possible exception of copper porphin. This suggests that in pyrrole the  $3135\text{ cm.}^{-1}$  band is to be assigned to an  $A_1$ ,  $B_1$  pair of alpha CH stretches while the  $3105\text{ cm.}^{-1}$  band is assigned to a corresponding pair of beta CH stretches.

The bands appearing at  $3041\text{ cm.}^{-1}$  (P) and  $3065\text{ cm.}^{-1}$  and the  $3045\text{ cm.}^{-1}$  shoulder (C) may be assigned to methylidyne CH stretching. The bands appearing at  $3029\text{ cm.}^{-1}$  and  $3054\text{ cm.}^{-1}$  in zinc tetraphenylporphin must then be assigned to phenyl CH stretching.

The bands at  $2852\text{ cm.}^{-1}$  and  $2930\text{ cm.}^{-1}$  (P) are in a region which is typical of methyl CH stretching but no CH bond of this type is present in porphin. The distinct reduction in the intensity of these bands in going from the sublimed film to the pressed window indicates that they do not represent compound absorption. The nature of the sublimation process is such that an impurity which is volatile compared to porphin would tend to concentrate in the film. For these reasons the  $2852\text{ cm.}^{-1}$  and  $2930\text{ cm.}^{-1}$



bands in porphin are assigned to an impurity, possibly a hydrocarbon. In etioporphyrin II, on the other hand both methyl and ethyl groups are present and the  $2862\text{ cm}^{-1}$ ,  $2928\text{ cm}^{-1}$ , and  $2965\text{ cm}^{-1}$  bands may be assigned to CH stretching in these groups.

The bands at  $3430\text{ cm}^{-1}$  (P window),  $3440\text{ cm}^{-1}$  (C) and  $3431\text{ cm}^{-1}$  (ZTP) are in a region typical of OH stretching. No band appears in this vicinity in either of the sublimed films, which suggests that this band may be a peculiarity of the pressed windows. In the process of making the windows it is necessary to grind the sample with potassium bromide. The large surface area of the powder would favor the adsorption of atmospheric water. Since the concentrations worked with are low, little water would need to be absorbed before bands comparable in intensity to the compound bands would be produced. In view of this the bands at around  $3440\text{ cm}^{-1}$  are assigned to OH stretching in adsorbed water.

A summary of these assignments, together with those for the region  $500\text{-}1500\text{ cm}^{-1}$ , is given in Table 9.

The reliability of the assignments given here is determined not only by internal consistency among the compounds discussed but also by agreement between the observed and predicted number and type of vibrations. The calculation based on  $D_{4h}$  symmetry gave 24 active modes

while that based on  $D_{2h}$  symmetry predicted 46. The number of fundamentals observed is 25, although it is probable that several more exist. This result indicates that the assumption of  $D_{4h}$  symmetry is an excellent one.

A comparison may also be made on the basis of the internal coordinates. While it is not possible to assign vibrations in detail equal to that of the internal coordinates the comparison may be made by grouping the calculated and observed modes.

Type of Vibration	Number Calculated	Number Observed
CH stretching	3	3
CH IP bending	4	3
CH OP bending	2	2
IP modes	14	12
OP modes	5	3

As calculated the  $E_u$  and  $A_{2u}$  species contain 5 redundancies most of which are expected to be found in the torsions and in-plane bendings, here labelled OP and IP modes. While the calculations were made ignoring the imino hydrogens and while several out of plane modes may be missing, again the agreement is excellent.

TABLE 9  
ASSIGNMENTS FOR PORPHIN

<u>CM.<sup>-1</sup></u>	<u>Vibration</u>
580(C)	pyrrole ring OP bending
650	pyrrole ring IP bending
694	NH OP bending
720	pyrrole ring IP bending
731	pyrrole ring IP bending
746	C-C-C IP bending
773	pyrrole CH OP bending
795	C-C-C IP bending
841	pyrrole ring OP bending
855	C-C-C IP bending
900	C-C-C OP bending
951	methylidyne CH OP bending
969	C-C stretching
992	C-C stretching
1048	pyrrole CH IP bending
1057	pyrrole CH IP bending
1137	pyrrole C-N-C IP bending (NH IP bending)
1185	pyrrole ring IP bending
1237	methylidyne CH IP bending
1248	combinations
1282	
1315	

TABLE 9 (continued)

<u>CM.<sup>-1</sup></u>	<u>Vibration</u>
1357	pyrrole ring IP bending
1407	pyrrole ring IP bending
3312	NH stretching
3108	pyrrole CH stretching
3041	methylidyne CH stretching
3065	methylidyne CH stretching



## CONCLUSIONS

1. The infrared spectra of crystalline porphin, copper porphin, etioporphyrin II, and zinc tetraphenylporphin have been obtained in the region  $650\text{--}3500\text{ cm.}^{-1}$ .
2. These spectra have been analyzed with the use of characteristic frequencies and assumed molecular point groups to obtain assignments for the bands observed in porphin. The use of molecular symmetry rather than site or cell symmetry proved adequate to account for the number of bands observed.
3. The results are in good agreement with the assumption of a model of  $D_{4h}$  symmetry for the porphin molecule. The evidence of the infrared spectrum supports the belief that porphin consists of a single isomer with hydrogens bonded to opposite nitrogens, at least in the solid state.
4. An improved technique for the preparation of sublimed films has been developed.

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