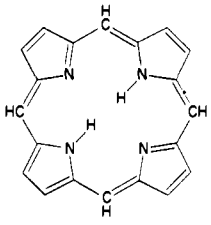
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY, ST. LOUIS]

A Spectroscopic Study of N-H Isomerism in Porphyrin Free Bases[1]

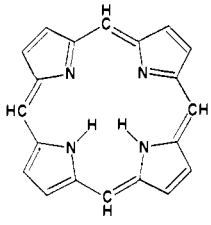
BY G. D. DOROUGH AND K. T. SHEN

I. The Porphin Free Base

The usual structure assigned to the porphin free base leads to two possible configurations for the center imino hydrogen atoms, one configuration with the hydrogens on opposite nitrogens (I), and the other with the hydrogens on adjacent nitrogens (II). No such isomers as these have ever been isolated despite the great number of

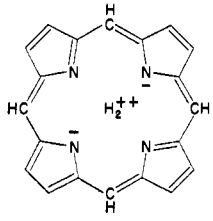


I



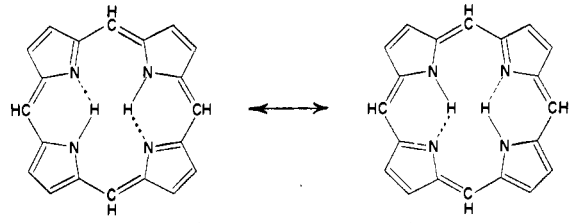
II

porphin compounds that have been investigated.[2] This fact can be attributed to one of two reasons: either the energy required for the tautomerism is too small ever to permit a physical separation of the two isomers, that is, they exist only as an inseparable equilibrium mixture, or else the hydrogen atoms are bonded in some entirely different manner which precludes the possibility of isomerism at all. The simplest structure in which the latter condition would be true is an ionic one (III); a more complicated structure, but one more favored in the literature, is some sort of resonant hydrogen bridge structure (IV) where the hydrogens occupy equivalent positions between two nitrogens. Such structures as III and IV, or indeed



III

any structures which do not permit N-H isomerism in the porphin free base, have as an essential feature imino hydrogens which are not bonded to single nitrogens in the normal covalent manner. Recent evidence of Corwin and Erdman,[3] however, indicates very strongly that the hydrogens are bonded normally. These authors observed



IV (Resonance structures)

that the absorption spectrum of a porphin in which one of the two imino hydrogens had been replaced by a methyl group was practically identical with the absorption spectrum of the corresponding unmethylated free base. The interpretation of this observation was that the two spectra would have been considerably different had the replaced hydrogen been bonded in any way but by a normal covalence, for the methyl group is most certainly bonded covalently. If this interpretation is accepted, then isomers I and II should exist, and it was the purpose of this work to attempt a demonstration of their existence.

If it is assumed that the porphin free base at room temperature is an equilibrium mixture of the two isomers I and II, then any spectrum measured at room temperature would be a composite of the individual spectra of the isomers. If the temperature should be lowered to that of liquid air or liquid nitrogen, the measured spectrum again would be a composite of the individual spectra, but the isomers will be in a different ratio to each other, since lowering the temperature will shift the equilibrium in favor of the more stable of the two forms. Finally, if the individual spectra of I and II differ sufficiently from one another, then the composite spectrum of the mixture measured at room temperature will not be the same as the spectrum measured at the very low temperature.[4] These considerations apply equally well to both absorption and emission spectra.

We have carried out the experiment the previous paragraph suggests, using as the porphin the free base of $\alpha,\beta,\gamma,\delta$-tetraphenylporphin. Absorption spectra at room and liquid air temperatures are plotted in Fig. 1; fluorescence spectra at room and liquid nitrogen temperatures are plotted in Fig. 2. It is seen that some rather marked changes in both types of spectra have occurred in going from room to very low temperatures. In the absorption spectra, for example, the two long wave length bands have shifted toward the blue, while the short wave length bands have shifted toward the red. The relative heights of the bands in the absorption spectra have been altered, and most of

(1) First in a series on "Fundamental Properties of Porphyrin Systems."

(2) The reported isolation of such isomers by Rothemund, THIS JOURNAL, **61**, 2912 (1939); **63**, 267 (1941) has since been shown to be incorrect: Pruckner, *Z. physik. Chem.*, **A190**, 101 (1942), and Ball, Dorough and Calvin, THIS JOURNAL, **68**, 2278 (1946).

(3) Corwin and Erdman, *ibid.*, **68**, 1885 (1946).

(4) A somewhat similar investigation of isomers of the crystal violet ion has been reported by Lewis, Magel and Lipkin, THIS JOURNAL, **64**, 1774 (1942).

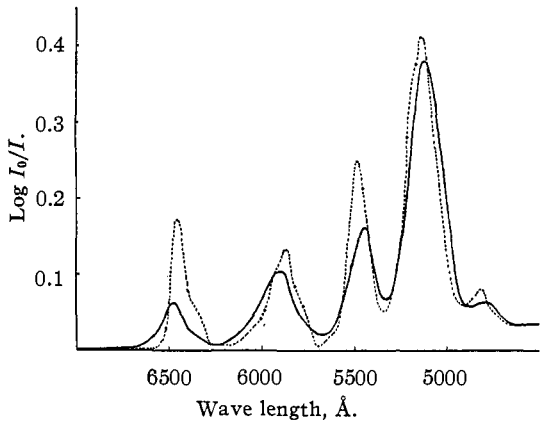


Fig. 1.—Absorption spectra of tetraphenylporphin free base in E. P. A.: solid line, room temperature; dotted line, liquid air temperature.

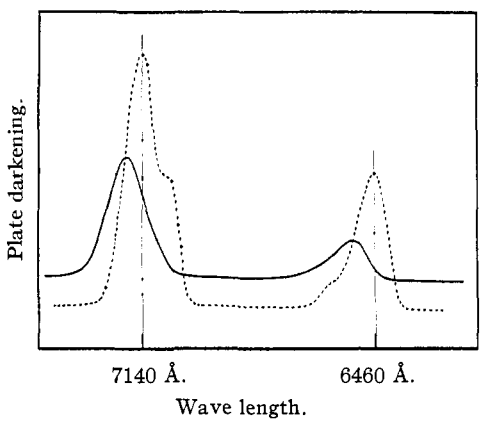


Fig. 2.—Fluorescence spectra of tetraphenylporphin free base in E. P. A.: solid line, room temperature; dotted line, liquid nitrogen temperature. The two curves were not traced to the same base line.

the bands in both types of spectra at the low temperature show definite signs of the fine structure which is just barely evident at room temperature, (see particularly the fluorescence spectra).

In marked contrast to the behavior of the free base is the behavior of porphin salts under similar conditions. The absorption spectra of the Ag(II) and Sn(II) salts of tetraphenylporphin (Figs. 3 and 4), and the fluorescence spectrum of the zinc salt (Fig. 5), show only a slight enhancement and sharpening of the band structure as the temperature is lowered; there is no shifting of bands, no evidence of fine structure. Since isomeric salt structures are impossible due to the fact that these divalent metals are bonded equivalently to all four center nitrogens, these spectral results establish definitely that the free base behaves unlike known non-isomeric structures, and suggest that the free base spectrum is actually a composite of more than one spectrum.

There is another important fact concerning free base spectra. The fine structure which is

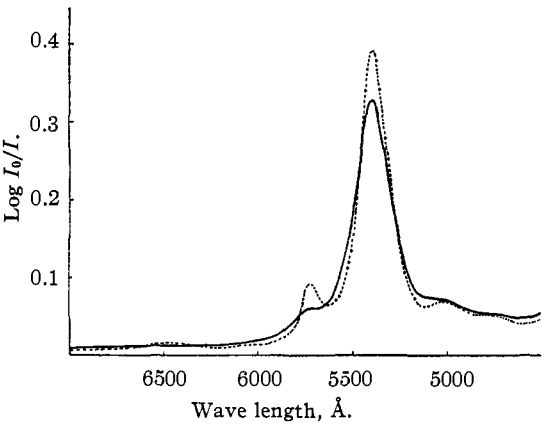


Fig. 3.—Absorption spectra of the Ag(II) salt of tetraphenylporphin in E. P. A.: solid line, room temperature; dotted line, liquid air temperature.

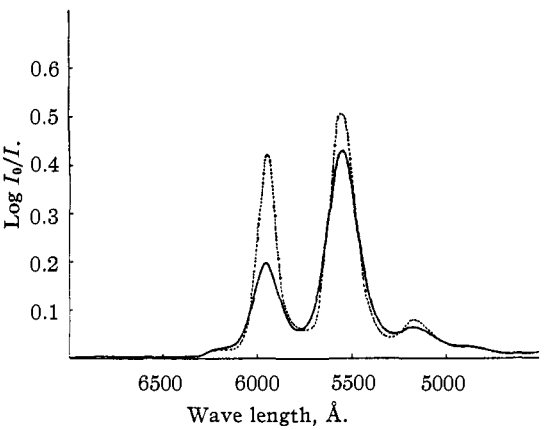


Fig. 4.—Absorption spectra of the Sn(II) salt of tetraphenylporphin in E. P. A.: solid line, room temperature; dotted line, liquid air temperature.

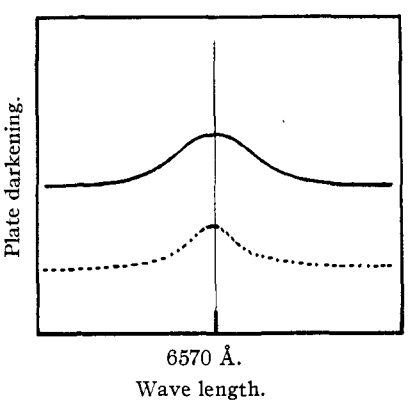


Fig. 5.—Fluorescence spectra of the zinc salt of tetraphenylporphin in E. P. A.: solid line, room temperature; dotted line, liquid nitrogen temperature. The two curves were not traced to the same base line.

readily apparent at low temperatures consists of small bands which taken together make up the unsymmetrically shaped large bands. Now the

spacing of these small bands varies considerably, but the range is about 130 to 240 cm.$^{-1}$. If these small bands belong to the same molecule, it is difficult to understand such an energy difference, for it is much too large for a rotational transition, and is much too small for a normal vibrational transition. It might conceivably be some slow vibration involving the whole ring, but if this were the case, the question arises as to why such a vibration is not observed in the salts. The best answer seems to be that these small bands do not belong to the spectrum of a single molecule, but arise from the overlapping spectra of more than one substance. Although not conclusive, here is further evidence that the porphin free base is an isomeric mixture.

Fortunately, emission spectra provide an experimental method for obtaining information concerning whether or not a given set of absorption bands are due to one or more absorbing substances. The fluorescence spectrum of an organic substance is as characteristic as is its absorption spectrum, and for most organic molecules is independent of the excitation leading to the fluorescence due to the fact that the fluorescence emanates only from the ground levels of the first excited state. This means that for a given set of absorption bands belonging to one substance, excitation of the molecule by absorption in any one of them will result in the same fluorescence spectrum. Thus, if we have two absorption bands which are due to two different substances, we can excite with monochromatic light in each of the two bands, and we will obtain different fluorescence spectra with each excitation. The application of this to the porphin free base is obvious; if we should compare fluorescence spectra of the porphin free base obtained by excitation with monochromatic light in different parts of the fine structure which make up a total absorption band, we would observe differences in these fluorescence spectra if the fine structure really were due to the overlapping of bands belonging to more than one substance.

We chose the large absorption band in the region of 6000 Å. for excitation. Figure 6 shows this absorption band and an estimate of the small bands of which it is composed (dotted bands). The distance between the two solid perpendicular lines represents the spectral width of one exciting light (X); the distance between the two dotted perpendicular lines the spectral width of a second exciting beam (Y). In Fig. 7 are shown the corresponding fluorescence spectra, the solid line representing a tracing of the fluorescence obtained with exciting light X, and the dotted line that obtained with exciting light Y. The two curves were traced with the bands at A arbitrarily set at the same height. It is seen that as the exciting light is shifted from X to Y, there is a definite decrease in emission at B and C, and a definite increase in emission at D. The effect is a gradual one, that is, if the wave length position of the exciting light is intermediate between that of X and Y, the fluorescence spectrum obtained is intermediate in every detail between the two curves shown in Fig. 7.

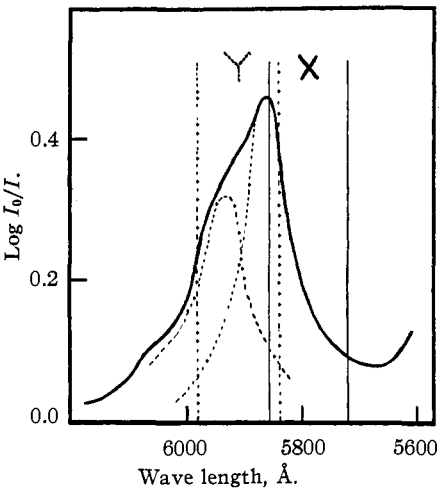


Fig. 6.—Second absorption peak of tetraphenylporphin free base in E. P. A. at liquid nitrogen temperatures: spectral band width of exciting light X 5720 to 5860 Å.; spectral band width of exciting light Y, 5840 to 5980 Å.

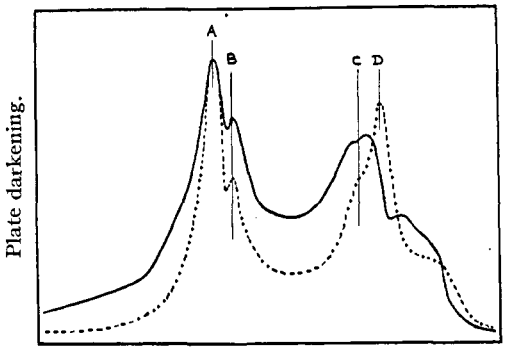


Fig. 7.—Fluorescence spectra of tetraphenylporphin free base in E. P. A. at liquid nitrogen temperatures: solid line, exciting light X (Fig. 6); dotted line, exciting light Y (Fig. 6); wave lengths, A, 7140 Å., B, 7000 Å., C, 6550 Å., D, 6460 Å.

It is unfortunate that there is so much overlapping in these fluorescence spectra. This is unavoidable, however, due in part to the fact that it is very difficult to hold the monochromatic character of the exciting light to close limits and still have sufficient intensities with which to work. Despite this difficulty, the dependence of the fluorescence upon the exciting light is quite apparent, and this is evidence that more than one species is contributing to the absorption or fluorescence spectra of Figs. 1 and 2. This leaves open, however, the question of whether or not these species are the isomeric structures I and II.

To answer this, let us consider one obvious alternate explanation. Suppose the diethyl ether

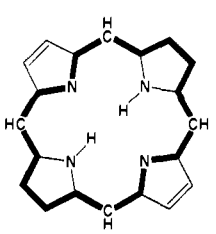
or ethanol in the E.P.A. solvent (see experimental) were to complex with the porphin free base according to some reaction like the following

$$PH_2 + EtOH \rightleftarrows PH_2 \cdot EtOH$$

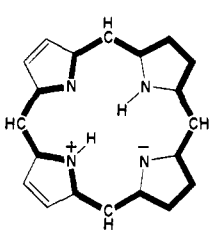
where PH_2 is the free base and $PH_2 \cdot EtOH$ is its complex. The species responsible for the composite spectra could then be the complexed and uncomplexed porphin free bases. We repeated the experiments shown in Figs. 1 and 2 using as a solvent a substance with very little complexing tendency, methylcyclohexane. Very similar curves to those in E.P.A. were obtained, indicating very strongly that the phenomenon is a property of the solute and is independent of the solvent. If this is so, the explanation offered by the equilibrium existence of isomeric structures I and II seems to be the most reasonable.

II. Resonance in the Porphin Free Base

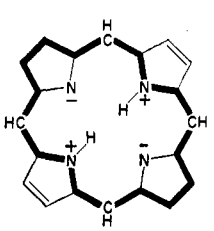
With the bonding of the imino hydrogens somewhat better established, it is perhaps worthwhile to discuss briefly resonance in the porphin free base, and the actual structure of the resonance hybrid. The structures shown in I and II for the porphin free base isomers are structures which represent the actual molecules no more closely than a single Kekulé structure represents benzene. Considering only the isomer with oppositely placed hydrogens, contributing resonance forms A, B and C may be written. The heavy line in these diagrams indicates the path of the single-double bond conjugated system. A few minutes



A. (Two forms resulting from alteration of single and double bonds)



B. (Eight forms resulting from alteration of single and double bonds and charges)



C. (Two forms resulting from alternation of single and double bonds)

inspection reveals that there are two equal energy forms of Type A, eight of type B, and two of type C. Due to the energy required for the separation of charges, the order of increasing energy of the forms is A, B and C. The relative contribution of the various types to the ground state is very difficult to calculate, but assuming that exchange integrals between wave functions representative of resonance forms for each type are approximately equal, simplified quantum mechanical treatment indicates that type B forms probably contribute at least as much to the ground state as the lower energy type A forms. Type C forms contribute appreciably only to the excited states. These considerations lead to the conclusion that the imino hydrogens lie out of the plane of the ring at an angle somewhere between 29° and 58°, the 29° corresponding to the angle the hydrogens would have if the free base were represented solely by type B forms, and the 58° to the angle if the free base were represented solely by type A forms.

There is considerable evidence which is in agreement with a large contribution of type B forms to the ground state. The amphoteric properties of the free base constitute one example. With a strong base such as sodium hydroxide or sodium methylate, the free base readily forms a sodium salt with the replacement of the two imino hydrogens, and with a strong acid such as hydrochloric, it forms an acid salt with the addition of two extra protons to the center of the ring. The charge separation resulting from type B forms accounts in part for these amphoteric properties, the relatively high K_a being attributed to the repulsion of the imino protons by the positive charges on the imino nitrogens, and the appreciable K_b being attributed to the attraction of two protons by the other nitrogens which are negatively charged.

The data of Vestling and Downing[5] on the position of N–H bond absorption in the infrared is also compatible with a large contribution of type B structures. They found the N–H band in pyrrole appeared at 2.85 μ, while etioporphin I free base gave a value of 3.01 μ. The shift toward lower energy would be in agreement with the weakening of the N–H bond due to the enhanced positive charge on the imino nitrogen, and the attraction of the proton by adjacent negatively charged nitrogens (weak hydrogen bond formation). The fact that an infrared N–H band is present close to its normal position shows that there is no strong hydrogen bonding in the porphin free base, a fact which is in agreement with and could have been predicted from the resonance hybrid composed of type A and B forms, for the positions of the imino hydrogens in this hybrid are in definite violation of the general observation that strong hydrogen bonds are formed only when the binding proton is directed more or less along the axis connecting the two bound atoms.[6] Since the hydrogens project out from the ring, a strong hydrogen bond is not possible.

A resonance hybrid of type A and B forms suggests something about the over-all shape of the porphin free base. Type B forms lead to a completely symmetrical structure with all C–N bonds

(5) Vestling and Downing, THIS JOURNAL, **61**, 3511 (1939).

(6) Pauling, "Nature of the Chemical Bond," Chapter IX, Cornell University Press, Ithaca, N. Y., 1940.

of equivalent length. Type A forms, however, lead to a somewhat elongated structure due to the fact that the four C–N bonds in the pyrroles with the imino hydrogens are longer than the other four C–N bonds. The resulting hybrid, then, should also be distorted, the amount of distortion depending on the relative contribution of type A forms. (The distortion in the free base with adjacent hydrogens would be even greater due to the unsymmetrically placed charge separation.) This, perhaps, is a better explanation of the distortion Robertson[7] found in the closely related phthalocyanine free base than the one offered of hydrogen bond formation.

The porphin free base is stabilized by resonance to the extent of about 250 kcal./mole below the classical structure of type A as calculated from heat of combustion data given for several free base porphins by Fischer and Orth.[8]

III. Other Porphyrin Free Bases

Absorption spectra of the free base of $\alpha,\beta,\gamma,\delta$-tetraphenylchlorin[9] and the deuterium free base of $\alpha,\beta,\gamma,\delta$-tetraphenylporphin (a free base in which the two imino hydrogens have been replaced by two deuteriums) have been measured at room and liquid air temperatures. The same type of spectral changes as were observed in the porphin free base are evident, the effect being particularly noticeable in the deuterium free base (see Figs. 8 and 9.)

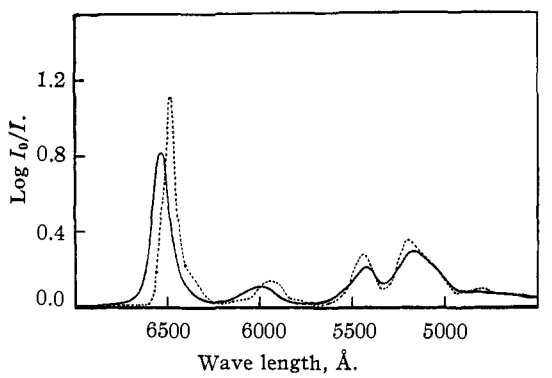


Fig. 8.—Absorption spectra of tetraphenylchlorin free base in E. P. A.: solid line, room temperature; dotted line, liquid air temperature.

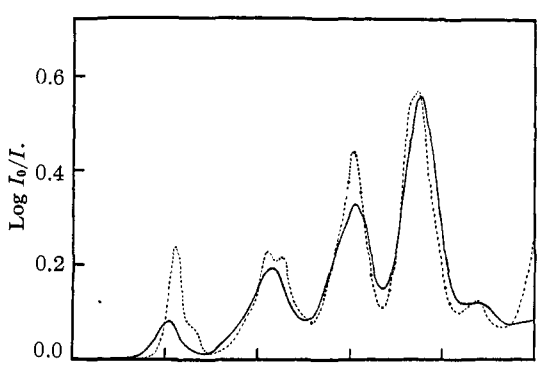


Fig. 9.—Absorption spectra of tetraphenylporphin deuterium free base in E. P. A.: solid line, room temperature; dotted line, liquid air temperature.

Acknowledgment.—Our appreciation is extended to Professor S. I. Weissman for the invaluable suggestion for the fluorescence experiments with monochromatic light.

Experimental

Part 1. Absorption Spectra

Apparatus.—The spectrophotometer used for absorption data was a Beckman Quartz Spectrophotometer, Model DU, fitted with a special cell compartment (see Fig. 10) to permit measurements at liquid air temperatures. This special cell compartment contained a silvered Pyrex glass Dewar flask with a window in the silvering for the passage of the light beam. The absorption cells containing the solution and the solvent were placed inside the Dewar on a specially mounted holder which permitted their being placed alternately in the light beam. The Dewar was left empty for room temperature measurements, and filled with liquid nitrogen or liquid air for low temperature work. The absorption cells were completely immersed in the cooling agent. Because of liquid oxygen absorption in the visible, liquid nitrogen is far superior for this work, but at the time these experiments were undertaken, liquid nitrogen was not always readily available in St. Louis.

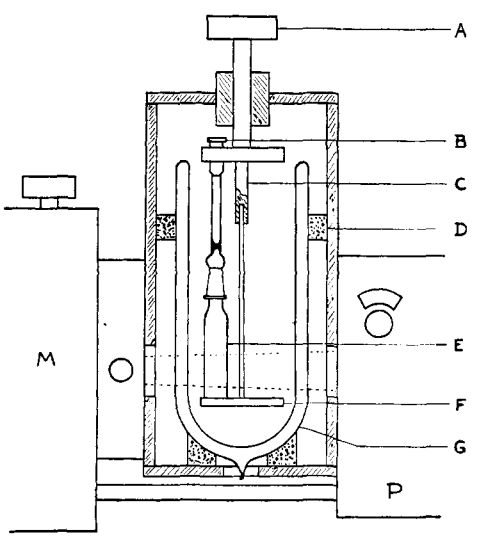


Fig. 10.—Cell compartment: A, cell position control knob; B, spring pin for holding cell; C. support for cell table (only one of three shown); D. cork spacers; E. 10-mm. Pyrex cell; F, cell table; G, Pyrex Dewar flask; M, Beckman monochromator compartment; P, Beckman photocell compartment; dotted lines, path of light beam.

Solvents.—The solvents for all absorption measurements were either an ether, isopentane, alcohol mixture in

(7) Robertson, *J. Chem. Soc.*, 1195 (1936).

(8) Fischer and Orth, "Die Chemie des Pyrrols," Vol. II, p. 599.

(9) The chlorin corresponds in structure to the porphin except that a double bond on the back of one of the pyrrole rings is reduced by the addition across the bond of two hydrogen atoms. A chlorin is thus a dihydroporphin.

the ratio of 5 to 5 to 2 (called E. P. A.),[10] or methylcyclohexane. These solvents do not crystallize on cooling, but freeze to clear glasses.

Icing.—Considerable difficulty was experienced in the early experiments because of ice or carbon dioxide particles crystallizing out on the optical faces of the absorption cells or the inside of the Dewar. A very thin coat of silicone oil 703 rubbed on the optical faces proved effective in preventing this difficulty (suggested by Professor D. Lipkin). Careful evacuation of the Dewar prevented frosting on the outside wall.

Spectral Curves.—All the spectral curves shown represent smooth curves drawn through points taken at 50 Å. intervals by even fifties.

Concentration Effect.—All sets of spectral data at room and liquid air temperature were taken on the same solution. The data at liquid air temperature, however, had to be corrected due to the fact that the solvents contract on freezing, and thus change the concentration. The correction factor for E. P. A. is 0.76.

Part 2. Fluorescence Spectra

Apparatus.—The apparatus centered about a Steinheil (München, Germany) three prism glass spectrograph. For spectra such as that shown in Figs. 2 and 5, the sample was placed in an unsilvered Dewar flask, and illuminated with a G. E. AH-6 mercury arc (midget sun) filtered by a 2" water filter to cut down the heat and by a Corning 5543 filter to remove any red light. The fluorescence light was filtered by a Corning filter 3480 to remove the exciting light, and focused on the slit of the spectrograph by a suitable lens arrangement. The spectrograph was equipped with entrance slits (fishtail type) which permitted both the room and liquid nitrogen pictures to be taken without moving the plate settings. This made possible comparative pictures which were independent of any small errors in wave length calibration. The plates were calibrated for wave length from a mercury spectrum using Hartmann's formula.[11] The spectra in Fig. 2 were photographed with an extra long arm on the exit side of the spectrograph, accounting for the excellent dispersion obtained for these curves.

For the curves shown in Fig. 7, the exciting light from the midget sun was first passed through a monochromater of the Littrow type.[12] The limiting wave lengths (spectral band width) of the resultant monochromatic light were determined by photographing the light on a calibrated plate in the Steinheil spectrophotometer. Fluorescence was excited with this light in the usual way. The fluorescence was focused on the entrance slits of the Steinheil, any exciting light being removed by a Corning filter 2408. Due to the drastically lower intensity of the exciting light in these experiments, a short arm was employed on the exit side of the Steinheil, thus making the dispersion considerably less than that obtained with the longer arm. Exposure times for these experiments with monochromatic light and the short exit arm on the spectrophotometer were about 8 hours; for the experiments with direct midget sun excitation and the long exit arm on the spectrophotometer about 10 minutes.

Solvents.—The same solvents were used as those employed for absorption work (E. P. A. and methylcyclohexane).

Icing.—Icing in the interior of the Dewar flask was prevented with silicone 703 as in the absorption work. Outside frosting on the unsilvered Dewar was prevented by an air stream directed against the portions of the flask where the light passed.

Plates.—All photographs were made on Kodak spectroscopic plates I-M, hypersensitized by treating with a 4% solution of 28% ammonia just before use.

Tracings of Spectral Plates.—The spectral plates were traced on a photoelectric densitometer. The curves shown in Figs. 2, 5 and 7 are direct reproductions of these tracings.

(10) Lewis, Magel and Lipkin, THIS JOURNAL, **62**, 2973 (1940).

(11) Sawyer, "Experimental Spectroscopy," Prentice-Hall, New York, N. Y., 1944, p. 230.

(12) We wish to express our appreciation to Professor S. Velick of the Washington University Medical School for the loan of this instrument.

Summary

1. Evidence has been obtained from an examination of absorption and fluorescence spectra taken at room and liquid air–liquid nitrogen temperatures which supports the proposition that porphin free bases exist as equilibrium mixtures of compounds resulting from the tautomerism of the imino hydrogens.

2. Absorption spectra at room and liquid air temperatures of a chlorin free base and a deuterium porphin free base are interpreted as indicating that the same tautomerism is present in these porphyrin free bases.

3. Resonance in the porphin free base is discussed, and a reasonable structure for the resonance hybrid is presented.

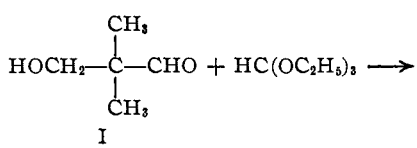
ST. LOUIS, MISSOURI RECEIVED NOVEMBER 30, 1949

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reaction of Hydroxyaldehydes with Ethyl Orthoformate. II. β-Hydroxyaldehydes

BY ELLIOT R. ALEXANDER AND ELLIOT N. MARVELL[1]

In an earlier communication,[2] it was shown that the reaction of hydroxypivaldehyde (I) with ethyl orthoformate led to 3,3-diethoxy-2,2-dimethylpropyl formate (II) as the only product which



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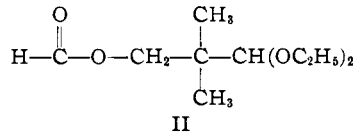

II

could be isolated. Furthermore, this product appeared to arise from the direct interaction of the hydroxyaldehyde with ethyl orthoformate and not as a secondary reaction product of hydroxypivaldehyde diethylacetal. In this paper is described a study of the reaction with several other β-hydroxyaldehydes.

(1) Oregon State College, Corvallis, Oregon.

(2) Alexander and Marvell, THIS JOURNAL, **71**, 15 (1949).