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The Interpretation of Porphyrin and Metalloporphyrin Spectra[1]

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Abstract: Spectral data from metalloporphyrin–ligand complexes show shifts in maxima which are significantly larger for the B (Soret) transitions than for the Q (visible) transitions, in contrast to previous findings not involving ligands. The shifts in the B transitions are ascribed primarily to a stereoelectronic effect. The data suggest weaker configuration interaction than previously assigned. The possibility that visible absorption bands in porphyrins may be due to n → π^* and l → π^* transitions is considered. Evidence in favor of this interpretation is presented, based on the examination of the spectra of monoprotonated porphyrins and on spectra in fluorosulfonic acid–antimony pentafluoride solution. Other possible interpretations of the data are also discussed.

It is generally agreed that the absorption bands of porphyrins and metalloporphyrins observed in the region 350–700 mμ are due to $\pi \rightarrow \pi^*$ transitions. Simple Hückel calculations by Longuet-Higgins, Rector, and Platt[4] assign the degenerate pair of e_g orbitals as lowest empty orbitals and a_{2u} and a_{1u} as highest and next highest filled orbitals, respectively. The near-ultraviolet absorption (Soret band) is then ascribed to a transition of the type $a_{1u} \rightarrow e_g$, while the visible bands are ascribed to $a_{2u} \rightarrow e_g$ transitions. This theory regards both transitions as allowed and does not account for the large difference in intensity observed between the visible and ultraviolet transitions. Platt[5] has modified this one-electron approach by assuming strong configuration interaction between a_{1u} and a_{2u} components. These are supposed to be nearly degenerate and give a combined "f" orbital, in Platt's notation, which has angular momentum of 4 au. The transitions from this orbital to the "g" orbital (e_g), having an effective angular momentum of 5, involve addition and subtraction of angular momenta giving rise to two degenerate states, B and Q, which separate by electron interaction. Transitions to the Q state (lower energy) are only weakly allowed owing to the large change in momentum involved, while transitions to the B state are strongly allowed and should be intense.

Gouterman has treated the porphyrins as 16-membered cyclic polyenes with the top filled states accidentally degenerate.[6] Considerations of this model lead to the same prediction of a weakly allowed visible band (Q band) of low intensity and a strongly allowed transition (B band) in the near-ultraviolet. Both Gouterman and Platt base their theories on strong configuration interaction between the top filled orbitals of the porphyrin. According to their models, behavior of the visible bands should be nearly identical with behavior of the Soret band for metalloporphyrins, with the only difference being in the intensities of the two transitions. Gouterman states that, since changes in the central metal atom of metalloporphyrins produce

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(1) (a) Part XXXVII of Porphyrin Studies; for part XXXVI, see E. W. Baker, A. H. Corwin, E. Klesper, and P. E. Wei, *J. Org. Chem.*, 33, 3144 (1968). (b) This work was supported by Research Grant GT-AM-02877 of the National Institutes of Health, U. S. Public Health Service.

(2) University of North Carolina, Chapel Hill, N. C.

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(4) H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, **18**, 1174 (1950).

(5) J. R. Platt, "Radiation Biology," Vol. III, A. Hollaender, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Chapter 2.

(6) M. Gouterman, *J. Chem. Phys.*, **30**, 1139 (1959); *J. Mol. Spectry.*, **6**, 138 (1961); M. Gouterman, G. H. Wagniere, and L. C. Snyder, *ibid.*, **11**, 108 (1963); M. Zerner and M. Gouterman, *ibid.*, **16**, 415, (1965); *Theoret. Chim. Acta*, **4**, 44 (1966); M. Zerner, M. Gouterman, and H. Kobayashi, *ibid.*, **6**, 363 (1966).

Table I. Absorption Band Energies for Metal Derivatives of Mesoporphyrin IX

	1 Mesoporphyrin IX derivatives	2 Solvent	3 Structure (ligands)	4 Q transition, cm^{-1}	5 ΔQ, cm^{-1}	6 B transition, cm^{-1}	7 ΔB, cm^{-1}	8 $E_B - E_Q$, cm^{-1}	9 ΔB − ΔQ, cm^{-1}
1	Nickel	Tetrahydrofuran	Tetragonal (0)	18,083	...	25,444	...	7361	...
1a	Nickel	Piperidine–THF	Octahedral (2)	17,421	−662	23,980	−1464	6559	−802
							Av	6960	
2	Copper	Tetrahydrofuran	Tetragonal (0)	17,761	...	25,188	...	7427	...
2a	Copper	Piperidine–THF	Square pyramid (1)	17,543	−218	24,449	−739	6906	−521
							Av	7166	
3	Cobaltous	Ethyl acetate	Tetragonal (0)	18,214	...	25,706	...	7492	...
3a	Cobalt hydroxide (III)	Pyridine	Octahedral (2)	17,793	−421	23,866	−1840	6073	−1419
3b	Cobalt acetate (III)	Acetic acid	Octahedral (2)	17,793	−421	24,390	−1316	6597	−895
							Av	6720	
4	Ferrous (low spin)	60% methanol 40% acetic acid	Octahedral (2)	17,953	...	25,062	...	7109	...
4a	Ferrous	Triethyl phosphite	Octahedral (2)	17,857	−96	22,831	−2231	4974	−2135
4b	Ferrous	Imidazole–phosphate buffer	?	18,348	+395	24,271	−791	5923	−1186
4c	Ferrous	Pyrrolidine	Octahedral (2)	18,315	+362	24,360	−702	6045	−1064
4d	Ferrous	Pyridine	Octahedral (2)	18,315	+362	24,360	−532	6215	−894
							Av	6053	
							Grand av	6556	

only small changes in porphyrin spectra, the interaction between the porphyrin and the metal is not very strong. He evaluates the effect of the two types of interactions between the metal and the porphyrin π-electron system, the inductive and the conjugative, and concludes that the metal d orbitals do not greatly affect the porphyrin π orbitals and consequently do not affect the metalloporphyrin spectrum. On symmetry grounds both p and d (t_{2g}) orbitals of transition metals can interact with e_g and a_{2u} orbitals of the porphyrin. Gouterman[6] showed that the energy difference between the first visible band and the near-ultraviolet band was roughly constant for some tetraphenylmetalloporphyrins. In later papers[6] he has applied the extended Hückel treatment to the calculation of porphyrin and metalloporphyrin spectra.

In an extensive investigation of metal mesoporphyrin IX complexes by Becker and Allison,[7] the authors published additional data supporting Gouterman's predictions of constant configuration interaction. They found a value of 7146 ± 256 cm^{-1} for the energy difference between the visible and near-ultraviolet transitions ($E_B - E_Q$). The slope for a plot of E_B *vs.* E_Q was unity. Metalloporphyrins having different spectra from the "normal" metalloporphyrin spectrum showed deviations from this value.

Our studies of metalloporphyrin complexes with additional ligands have led us to conclude[8] that, in addition to metal–porphyrin interactions considered by Gouterman, two other types of interaction must be considered: metal–ligand interactions and ligand–porphyrin interactions. Extensive studies on transition metal mesoporphyrin complexes have shown that both the visible and near-ultraviolet transitions are affected by stereoelectronic interactions between ligands bonded to the metal and the porphyrin π electrons.[8] The near-ultraviolet transition is shifted to longer wavelengths on interaction of the metalloporphyrin with strong ligands, the extent of the shift being dependent upon the number, size, and tightness of bonding of the ligands to the metal. Both visible transitions are also shifted in the systems studied. The shift is less in the visible than in the ultraviolet and may be in either direction energetically. The first visible transition decreases in intensity compared to the second. No significant increase in the intensity of the visible bands in relation to the near-ultraviolet peaks has been detected. Of the three types of interaction mentioned, we have found the ligand–porphyrin interaction to produce the largest effect on porphyrin spectra for several metalloporphyrins including zinc, copper, nickel, cobalt, and low-spin ferrous.

The availability of data on complexed and relatively uncomplexed metalloporphyrins gives us the opportunity to test Gouterman's predictions regarding configuration interaction from a slightly different point of view. Table I gives the transition energy differences for a number of complexed and uncomplexed transition metal derivatives of mesoporphyrin IX.

Column 8, labeled $E_B - E_Q$, corresponds to Becker and Allison's[7] value of 7146 ± 256 cm^{-1}. In this column, the largest positive deviation from 7146 cm^{-1} is 346 cm^{-1}. The largest negative deviation, on the other hand, is 2172 cm^{-1}, a substantial fraction of the total energy difference involved. This indicates that the ligand–porphyrin interaction is capable of affecting the energy difference between the B and Q transitions quite differently.

Analysis of columns 5 and 7 will show that, with a given metalloporphyrin, the effect of ligand–porphyrin interaction is greater on the B band and in this case is always negative, causing a shift of the transitions to lower energies. The effects on the Q bands, on the other hand, are smaller and may be in either direction. It is not clear how to predict the effects of external perturbations, such as those caused by ligands, on the

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(7) R. S. Becker and J. B. Allison, *J. Phys. Chem.*, **67**, 2675 (1963).

(8) D. G. Whitten, E. W. Baker, and A. H. Corwin, *J. Org. Chem.*, **28**, 2363 (1963); A. H. Corwin, D. G. Whitten, E. W. Baker, and G. G. Kleinspehn, *J. Am. Chem. Soc.*, **85**, 3621 (1963); E. W. Baker, M. S. Brookhart, and A. H. Corwin, *ibid.*, **86**, 4587 (1964); C. B. Storm, A. H. Corwin, R. R. Arellano, M. Martz, and R. Weintraub, *ibid.*, **88**, 2525 (1966).

Table II

	1 Compound	2 Solvent	3 Q transition, cm^{-1}	4 B transition, cm^{-1}	5 $E_B - E_Q$, cm^{-1}	6 $\Delta B - \Delta Q$, cm^{-1}
1	Zinc meso IX	Cyclohexane	17,637	25,253	7616	
2	Zinc meso IX	Picoline	17,271	24,213	6942	−674
3	Zinc meso IX	Pyrrolidine	17,182	24,155	6973	−643
4	Zinc meso IX	Carbon disulfide	17,379	24,183	6804	−812
5	Zinc meso IX	CS_2 and pyridine	17,082	23,359	6277	−1339
6	Zinc dicyanodeutero	Chloroform	16,995	23,585	6590	−1026
7	Zinc diformyldeutero	Chloroform	16,491	22,548	6057	−1559

interaction of configurations, but the effects are not consistent with the concept that interactions affecting the energy of the B transition will affect that of the Q transition essentially equally.

Caughey, Deal, Weiss, and Gouterman[9] have suggested that charge transfer might be found in transition metals with open d shells. If such a charge-transfer band were to mix with the B band, it should lower its energy. Such a mixing would have less effect on the Q band. Thus the possibility of the existence of such a charge-transfer band might be advanced as an explanation for the unequal effects of ligands on the B and Q bands. That such is not the case, however, can be learned from observations on zinc complexes, where the d levels are filled and such charge-transfer bands would not exist. Table II gives pertinent data for the shifts in a series of zinc complexes.

Since the energy shifts of column 6 in Table II are comparable in magnitude to those in column 9 of Table I, the hypothesis that the shifts are due to mixing of a charge-transfer band with the B and Q transitions is not tenable.

This laboratory has advanced the hypothesis that, in suitable cases, shifts in the Soret bands (B bands) can be correlated with the ligandcy of the metalloporphyrins and are due to a stereoelectronic effect.[8] This hypothesis is based on the concept that the size of the ring in the excited state, involving an antibonding orbital (e_g), is greater than that of the ground state. A schematic representation of the energy relationships is given in Figure 1.

The relationships in Figure 1 are consistent with the observed facts that two ligands shift the Soret band approximately twice as much as one and that larger ligands, like triethyl phosphite, shift the Soret band more than do smaller ligands, such as the nitrogen bases.[8] This is true even though the energy of ligation is smaller in the case of triethyl phosphite, as shown by the fact that it is readily replaced by nitrogen bases. We conclude that shifts in the Soret region caused by the addition of ligands provide a tool for the investigation of the energy relationships of the π cloud in the ground state and the excited state.

The fact that structural and ligand alterations can affect B transitions more than Q transitions makes a reexamination of the basic assumptions of the theory of the absorption spectra of porphyrins desirable. In particular, since techniques are now available for the quantum mechanical estimation of the energies of transitions involving nonbonded electrons, the possibility that some of the porphyrin transitions may be of this type merits reconsideration. Caughey, Deal, Weiss, and Gouterman[9] have stated that n → π* transitions might occur in the free base. We shall review herewith some of the experimental and theoretical considerations bearing on the possibility of the occurrence of transitions involving the nonbonded electrons of the porphyrin ring.

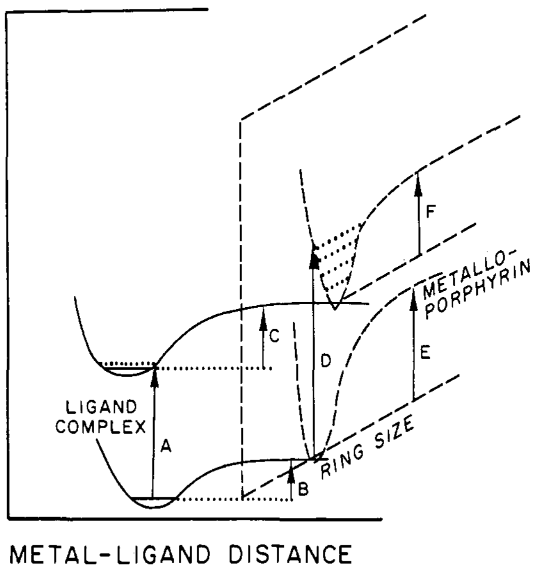

Figure 1. The stereoelectronic effect on the Soret band. In the potential diagram of the metalloporphyrin, a curve representing dissociation would correspond to a ring expansion to infinity. For this reason, the abscissa is chosen as ring size. Promotion of an electron from a bonding orbital to an antibonding orbital will expand the ring, displacing the equilibrium position of the potential curve to a higher value along the abscissa in the excited state. Because of the resultant weaker ring bonding, the dissociation energy of the excited state, *F*, will be less than that of the ground state, *E*. In the potential diagram of the ligand complex, the abscissa is chosen as the distance from the metal to the bonding heteroatom of the ligand. Complete dissociation of the ligand complex regenerates the metalloporphyrin, as indicated by the coincidence of the energy levels of these potential curves with the zero-point energies of the metalloporphyrin in the ground state and the excited state. In the ligand complex, the minimum of the potential curve of the excited state is at a smaller metal-to-ligand distance than in the ground state, because the ring expansion in the excited state creates less steric interference than in the ground state. Because of the closer approach of the heteroatom to the metal possible in the excited state, the dissociation energy of the excited state, *C*, is greater than that of the ground state, *B*. The transition energy of the metalloporphyrin, *D*, is greater than that of the ligand complex, *A*, because of this greater dissociation energy and because of the greater steepness of the potential energy curve on the compression side than on the expansion side. These two energy differences combine to give the stereoelectronic red shift observed in the formation of ligand complexes from metalloporphyrins.

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(9) W. S. Caughey, R. M. Deal, C. Weiss, and M. Gouterman, *J. Mol. Spectry.*, 16, 451 (1965).

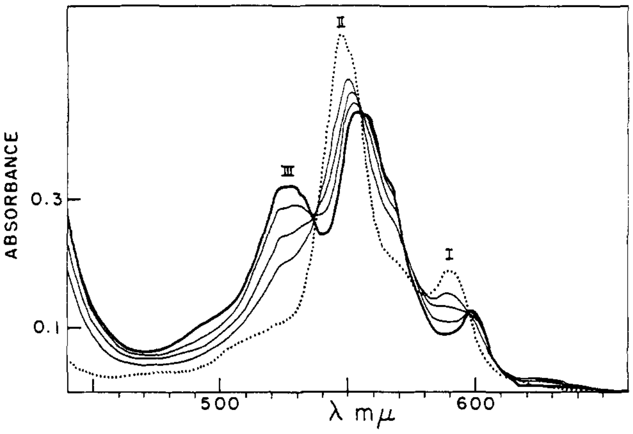

Figure 2. Porphyrin base (- - -) to porphyrin monohydrochloride (——).

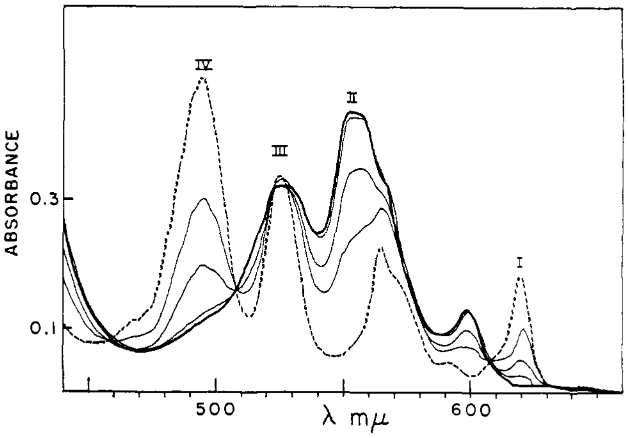

Figure 3. Porphyrin monohydrochloride (——) to porphyrin dihydrochloride (· · · · ·).

A porphyrin free base contains four pairs of "nonbonded" electrons. Two of these pairs are of the "pyrrole type" and two are of the "pyridine type." Using the notation of Kasha,[10] the pyrrole-type pairs are "l" orbital electrons and the pyridine-type pairs are "n" orbital electrons.

Kasha[10] and Sidman[11] have tabulated the criteria usually met by n transitions. One of these is a low transition probability. The high extinction coefficients of the visible bands of the porphyrin spectrum are, perhaps, the major objection to the assumption of n $\rightarrow \pi^*$ transitions for these absorptions. Kinds and degrees of forbiddenness have been discussed by Platt.[12] In the present instance, overlap forbiddenness is the chief cause for the reduction in intensity. The prototypes from which this reasoning was derived are aromatic azines. The n orbitals of porphyrins are significantly different from those of azines in two essential features, however. Goodman[13] has pointed out that overlap between nitrogen orbitals in polyazines increases their oscillator strengths. The two pairs of n electrons on opposite sides of the porphyrin ring would permit a type of overlap different from those in the azines. This would tend to delocalize the electrons in the ground state and increase the overlap with the excited state. In addition, because of the stereochemical difference between five-membered and six-membered rings, the s character of the n orbitals of the porphyrins would be less than that of the six-membered azines studied. These structural peculiarities of the porphyrin ring system render the aromatic azine models of doubtful applicability so that reasoning based on analogy with other n $\rightarrow \pi^*$ transitions need not apply here. In particular, the structural features giving greater overlap of the porphyrin n electrons with the π cloud could well increase the probability of an n $\rightarrow \pi^*$ transition by a substantial amount over that of any other heterocyclic system which has been studied.

A second criterion for an n $\rightarrow \pi^*$ transition is the disappearance of the absorption band ascribed to such a transition by solution in an acidic medium. It is well known that porphyrin dihydrochlorides have two major bands of the free bases missing. This has been ascribed by Platt[5] to the change in symmetry from D_{2h} to D_{4h} with concomitant degeneracy of the X and Y components of the visible bands. It could equally well be ascribed to bonding of the n electrons. Evidence bearing on this question may be obtained by reference to the spectra of monoprotonated porphyrins. Monoprotonated porphyrins were first described by Treibs.[14] They have been more fully investigated by Neuberger and Scott.[15] In 1941, Aronoff and Weast[16] attempted unsuccessfully to prepare the monocation of mesoporphyrin. We have found that the use of the dimethyl ester solves the difficulty. A simple method for the preparation is to dissolve the ester in 60% glacial acetic acid and 40% acetone.

If an increase in symmetry were responsible for the change on going from the free base to the diprotonated species, then there should be no decrease in spectral complexity on going to the monoprotonated species, since there is no increase in symmetry, rather the reverse. In fact, however, it is observed that the free base has four major visible absorption peaks, the monoprotonated species has three, and the diprotonated species has two. This is the behavior to be expected with successive protonation of the two "pyridine-type" nonbonded pairs of the free base.

The spectral curves intermediate between the free base and the monocation (Figure 2) reveal two isosbestic points in conjunction with the diappearance of band IV in the visible spectrum. Changes in band III during the protonation are minimal. Band I undergoes a shift from 620 to 599 mμ in the process. A similar shift and an increase in intensity occur for band II. Both bands I and II appear to be composite, formed from overlapping transitions. A more detailed experimental examination of these component transitions would be required to reach definitive conclusions concerning the nature of the changes observed.

By substitution of monobromopropionic acid for acetic acid in 40% acetone, conversion of the monocation to the dication can be secured. The intermediate spectral curves (Figure 3) show that this protonation removes band III. The second proton-

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(10) M. Kasha, "Light and Life," W. D. McElroy and B. Glass, Ed., The Johns Hopkins Press, Baltimore, Md., 1961, p 31.

(11) J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).

(12) J. R. Platt, *J. Opt. Soc. Am.*, 43, 254 (1953).

(13) L. Goodman, *J. Mol. Spectry.*, **6**, 109 (1961).

(14) A. Treibs, *Ann.*, **476**, 1 (1929).

(15) A. Neuberger and J. J. Scott, *Proc. Roy. Soc.* (London), A213, 307 (1952).

(16) S. Aronoff and C. A. Weast, *J. Org. Chem.*, **6**, 550 (1941).

ation increases the intensity of band II but causes only a small shift in its wavelength maximum. This appears to be due to the removal of a hump on the low-energy side. However, in the case of band I, another conversion similar to that observed on monoprotonation occurs. Thus band I of the dication has resulted from two successive stepwise shifts from band I of the free base.

The monoprotonation experiment does not definitely rule out a $\pi \rightarrow \pi^*$ transition for band IV. It may be argued that the first protonation of the free base has merely shifted band IV so that it now falls under band II, thus causing the observed increase in intensity of band II. If this were the case, the apparent diminution in spectral complexity would really be masking the formation of a composite band. This argument is difficult to deal with experimentally, since the original bands of the free base are already composite, and a still greater degree of complexity of the bands would require more refined methods of band analysis for its clarification. Although the experiment is thus not definitive, it is consistent with the hypothesis of an $n \rightarrow \pi^*$ transition for this band.

A third characteristic of $n \rightarrow \pi^*$ transitions is the so-called "conjugative-substituent" blue shift discussed by Goodman and Harrell.[17] Goodman and Harrell select as their "primarily conjugative" substituents, CH_3, Br, and Cl, a classification which is not in agreement with substituent effects obtained by organic chemical means.[18] Using six-membered nitrogen heterocycles, they observe that, in nearly all cases, $n \rightarrow \pi^*$ transitions undergo blue shifts of 0–5900 cm^{-1} while in the same systems $\pi \rightarrow \pi^*$ transitions undergo red shifts of 700–6100 cm^{-1}. The "conjugative blue shift" is rationalized on the grounds that the $n \rightarrow \pi^*$ transition tends to transfer negative charge from the heterocyclic nitrogens to the π system and that this effect would be opposed by a substituent which was itself an electron donor, thus raising the energy required for the transition in the presence of the substituent.

Substitution of two bromines for two hydrogens in deuteroporphyrin produces small red shifts in the range of 121–155 cm^{-1} in the visible and Soret bands.[19] Substitution of two ethyl groups produces red shifts in the range of 28–109 cm^{-1}.[20] These changes are small enough to be ascribed wholly or in part to changes in zero point energy and are thus not diagnostic for the type of transition involved.

There is a reasonable basis for the contention that the analogy based on blue shifts observed for some $n \rightarrow \pi^*$ transitions and red shifts observed for some $\pi \rightarrow \pi^*$ transitions need not be generally valid. Azine rings of the type studied by Goodman and Harrell are electron-attracting structures and would be expected to attract electrons from substituent bromines and methyls. Porphyrin rings, on the other hand, are electron-donating structures and would be expected to donate electrons inductively to bromines. Studies on zinc porphyrins in this laboratory[21] indicate that Hammett's equation is followed in this case. This would place bromine as an electron acceptor and methyl or ethyl as a weak, nearly isopolar electron donor with respect to ***hydrogen***. The polarity of the porphyrin ring with respect to hydrogen is indeterminate, however. Arguing on the grounds of the spectral shifts observed, one would conclude that ethyl is electron accepting with respect to the porphyrin ring and, therefore, that hydrogen is also electron accepting in this system. Thus, following the type of reasoning advanced by Goodman and Harrell for the azines, the reversal of polarity of the bromines with respect to the ring in the case of porphyrins should cause a distinct red shift, as observed. The postulated small reversal of polarity in the case of ethyl should cause a small red shift, as observed. Hence the direction of the shift caused by these substituents ceases to be diagnostic for the type of transition.

Still another characteristic of $n \rightarrow \pi^*$ transitions is the blue shift in polar solvents.[10] Using isooctane as the solvent of low dielectric constant and ethanol as the more polar medium, bands I and II and the Soret in mesoporphyrin dimethyl ester undergo blue shifts in the more polar solvent. Bands III and IV undergo red shifts. Again the magnitude of the shifts is minimal, 44–159 cm^{-1}. In this case the red shifts may be completely ascribed to changes in refractive index.[22] The blue shifts, as stated above, are of such small order of magnitude as to provide no supporting evidence for the concept of $n \rightarrow \pi^*$ transitions. Thus the evidence based on solvent polarities is neutral, as is that based on substituent effects presented above.

Another characteristic of $n \rightarrow \pi^*$ transitions is fluorescence quenching in the cases in which these are the lowest energy transitions. The strong fluorescence emission of the porphyrin free bases and the possible assignment of band I as $n \rightarrow \pi^*$ is at variance with this criterion. Exceptions to the rule of fluorescence quenching are known, however.[23] These have been discussed and a theoretical explanation has been offered by El-Sayed.[24] Hence the presence of fluoresence constitutes no barrier to the acceptance of the concept of an $n \rightarrow \pi^*$ transition for band I of the porphyrin free base. In the metalloporphyrins, we argue that band I results from an $l \rightarrow \pi^*$ rather than an $n \rightarrow \pi^*$ transition.

We may conclude that the evidence reviewed above provides reasonable ground for a reexamination of the possibility that some of the absorptions bands of porphyrin free bases may result totally or in part from $n \rightarrow \pi^*$ transitions.

In the metalloporphyrins and the diprotonated species, n electrons of the free bases have been bonded but l or "pyrrole-type" electrons are still present. Bonding of these through protonation should result in a further simplification of the spectra of these materials, if our hypothesis that these electrons are responsible for all or part of the remaining visible absorption bands is correct. Such protonation should be achieved by dissolving these substances in very strong acids. The behavior of vanadyl mesoporphyrin in sulfuric acid has been recorded by Dean and Girdler,[25] and its spectrum

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(17) L. Goodman and R. W. Harrell, *J. Chem. Phys.*, 30, 1131 (1959).

(18) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 188.

(19) H. Fischer and H. Orth, "Die Chemie des Pyrrols," Vol. IIb, 2nd ed, Akademie-Verlag, Leipzig, 1937, pp 257, 416.

(20) A. Stern and A. Wenderlein, *Z. Physik. Chem.*, A174, 84 (1935).

(21) A. H. Corwin and G. McGrew, unpublished.

(22) G. R. Seeley and R. G. Jensen, *Spectrochim. Acta*, 21, 1835 (1965).

(23) M. Chowdhury and L. Goodman, *J. Chem. Phys.*, **36**, 548 (1962); **38**, 2979 (1963).

(24) M. El-Sayed, *ibid.*, **38**, 2834 (1963).

(25) R. A. Dean and R. B. Girdler, *Chem. Ind.* (London), 100 (1960).

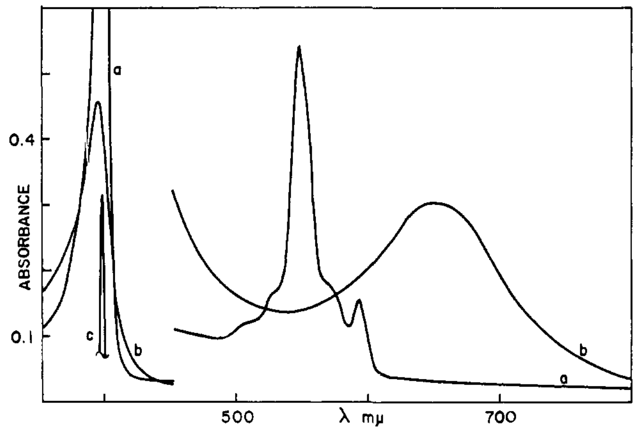

Figure 4. (a) Etioporphyrin II in HSO_3F. (b) Etioporphyrin II in HSO_3F after addition of a few drops of SbF_5. Spectra from 350 to 450 mμ are taken with reduction of the light path by a factor of 10. (c) The top of a, displaced 1.3 units on the ordinate to show the position of the maximum.

in methanesulfonic acid has been observed by Erdman.[26] They have observed, and we have verified, that these treatments result in a qualitative simplification of the visible absorption bands, leaving broad general absorption in the visible, while the Soret band remains, although its position is shifted to higher energies. Dilution of the solution with water restores the original spectrum. We have also observed this phenomenon with solutions of tin mesoporphyrin in sulfuric acid containing a few per cent sulfur trioxide. These latter spectral changes are only incompletely reversible, however. These observations fit those expected for protonation of the l electrons of the metalloporphyrin and are consistent with the hypothesis that protonation of the l electrons profoundly modifies the absorbing system responsible for visible absorption while leaving that responsible for the Soret band essentially intact.

Solution of porphyrin acid salts in sulfuric acid produces no change beyond that observed for the diprotonated species. When etioporphyrin II is dissolved in fluorosulfonic acid and antimony pentafluoride, the normal visible bands due to the diprotonated species disappear and are replaced by a single broad diffuse band centered at about 650 mμ (Figure 4). In this acid, the Soret band is shifted from 397 to 393 mμ, the band is broadened, and the extinction coefficient is lowered. Dilution with a small amount of water restores the spectrum of the diprotonated species. The solution of etioporphyrin in the HSO_3F–SbF_5 solution has a characteristic green color. We are investigating the structure of this green compound. Whatever its structure, it is clear that its formation, like those of the tin and vanadyl complexes in sulfuric acid, provides a disassociation of the transitions responsible for the visible bands from the $\pi \rightarrow \pi^*$ transition responsible for the Soret band. As a working hypothesis, we may assume that solution in HSO_3F–SbF_5 causes a reaction involving the weakly basic "pyrrole-type" lone pairs. Without more evidence, the extent of the delocalization of these l electrons is not accurately predictable. Independent evidence is available from intrinsic polarization studies made by Gurinovich, Sevchenko, and Solov'ev.[27]

The intrinsic polarization of fluorescence, also termed "fundamental," "basic," or "limiting" polarization, is defined[28] as the degree of polarization of the rotation-free molecule. It is estimated experimentally by measurement of the degree of polarization at a constant temperature in solvents of varying viscosity and extrapolating the values thus obtained to infinite viscosity. There is some variation in the degree of polarization with temperature. Because of solvent limitations, however, the Russian investigation was carried out by varying the viscosity of the solutions under study by means of temperature variations and then extrapolating to infinite viscosity.

Gurinovich, *et al.*,[27] have examined the intrinsic polarization of a number of metalloporphyrins. They find this to be 13%, corresponding to absorption and emission oscillators in the plane of the porphyrin ring and having D_{4h} symmetry.[28] They interpret this as indicating a $\pi \rightarrow \pi^*$ transition, but the data would fit equally well the case of an $l \rightarrow \pi^*$ transition, since the two are indistinguishable with respect to their planes. To belong to the D_{4h} symmetry group, however, these electrons, like π electrons, would have to be delocalized throughout an area involving all four pyrrole rings of the porphyrin system. It might be argued from this that the distinction between such l electrons and the π electrons is purely semantic. The spectroscopic observations in acid solution recorded above establish the distinction, however. Addition of protons to the π system to form a π complex would be expected to diminish the sharpness of the visible bands without causing a significant change in their positions or extinction coefficients.[29] Addition to the π system to form a σ complex should interrupt the conjugation, forming either a chlorin-like material, if the addition were β, or a phlorin-like material,[30] if the addition were α or on the methine bridge. The latter bear some resemblance to the colored σ complexes absorbing at lower energies than the aromatic hydrocarbons which are observed on protonation of these hydrocarbons.[29–31] Both chlorins and phlorins have absorption bands with high extinction coefficients in the red. Addition of protons to the l system, on the other hand, would form N–H bonds. The absorption bands due to the l electrons in the visible should then be replaced by new ones due to the N–H bonds, probably in the vacuum ultraviolet. The behavior actually observed on protonation of the metalloporphyrins is a disappearance of sharp visible absorption bands instead of the appearance of chlorin-like or phlorin-like bands. This contrasts to the behavior expected for the π electrons.

Gurinovich, Sevchenko, and Solov'ev[27] have also measured the intrinsic polarization of a number of porphyrin free bases. This is found to be 40%. This establishes the fact that band I of the porphyrin free bases has a different symmetry from band I of the metalloporphyrins. The hydrochlorides of mesoporphyrin and protoporphyrin have intrinsic polarization of 18%, a close approach to that of the metal-

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[26] J. G. Erdman, personal communication.

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[28] A. Jablonski, *Z. Physik*, **96**, 236 (1935).

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[30] R. B. Woodward, *et al.*, *ibid.*, **82**, 3800 (1960); D. Mauzerall, *ibid.*, **84**, 2437 (1962).

[31] H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

loporphyrins. Hence the two successive changes in band I observed in the stepwise conversion to the dihydrochloride have altered the symmetry of the oscillator. For this we must conclude that a fundamental change occurred when this band was shifted in the protonation process.

A value of 40% for the intrinsic polarization can be obtained either from a planar elliptical oscillator, corresponding to D_{2h} symmetry, or from an out-of-plane polarization. Theoretically, then, the interpretation of the measurement is potentially ambiguous. The original investigators interpret the polarization to fit the accepted concept that the transition involved is a $\pi \rightarrow \pi^*$ transition and therefore in-plane. Actually, the ellipticity of the planar oscillator would have to be 0.995 to give 40% polarization. This is a close approach to a linear oscillator. There is no compelling reason for concluding that the relatively small departure from D_{4h} symmetry observed in the porphyrin free bases should give an ellipticity in which one oscillator is 21 times as great as the other. The alternative assumption is that the polarization is 23° out of plane, thus giving rise to the ambiguity of interpretation.

The interpretation of the results of polarization studies on band I of porphyrin free bases is rendered still more difficult because this band is not due to a single vibronic component but to three, as shown by the measurements of Rimington, Mason, and Kennard[32] at $-180°$ on porphin. It is not even certain that the three spectral components are due to the same molecular species, since Dorough and Shen[33] have advanced evidence for the existence of NH isomers in the porphyrins. These observations make all analyses of porphyrin polarization data much less certain.

Anex and Umans[34] have recently published a preliminary communication concerning the assignment of polarizations of the electronic transitions for a porphyrin free base. A more detailed description of the nature of the correlation between their polarization observations and the orientation of the crystals with respect to the porphyrin molecules may throw light on the question of the orientation of the transitions of bands III and IV. Their preliminary analysis seems oversimplified, however, since they have tentatively assumed that band I consists of a single vibronic component instead of the three found by Rimington, Mason, and Kennard.[32]

The resolution of the ambiguity with respect to the intrinsic polarization of band I is not important at the moment, since there is at present no certain method for predicting the direction of polarization to be expected for a porphyrin-type $n \rightarrow \pi^*$ transition. The same considerations of increased overlap with the π electrons and increased delocalization of the n orbitals which could permit these orbitals to assume enough π character to increase the extinction coefficients of their transitions could also act to alter their plane of polarization from the out-of-plane direction usually associated with $n \rightarrow \pi^*$ transitions toward an in-plane polarization. This probably renders the use of polarization measurements inapplicable to the problem of the determination of the nature of the transitions in the visible bands of the porphyrins.

We conclude that the fact that fluorosulfonic acid destroys the usual four-banded visible spectrum of porphyrin free bases without the formation of chlorin-like or phlorin-like bands and without destruction of the Soret band indicates that the species formed under these conditions still retains the absorbing system responsible for the Soret band, presumably the main conjugation of the porphyrin ring. At the same time, the absorbing systems responsible for the usual visible bands have been altered. Since the changes involved encompass bonding with n electrons first and then presumably with l electrons, the possibility is raised that the systems which are altered by combination with acid are the ones whose excitation is responsible for the visible absorption bands. The experimental fact that the fluorosulfonic acid solution has a qualitatively altered spectrum is sufficient to disassociate the absorbing systems responsible for the visible and Soret bands.

Experimental Section

The mesoporphyrin IX was prepared from hemin by the method of Baker, Ruccia, and Corwin[35] followed by esterification with diazomethane to give mesoporphyrin IX dimethyl ester.

The solutions for the acid titration of the mesoporphyrin IX ester, shown in Figures 2 and 3, were prepared by taking aliquots of a concentrated stock solution of the porphyrin, prepared in acetone, followed by dilution with acetone or acid to give the solutions of various volume per cents acid.

Spectra were recorded on Beckman DK-2 and Carey 14 spectrophotometers using matched 1-cm quartz cuvettes. Soret spectra were made with 9-mm quartz inserts.

Solutions in absolute ethanol and isooctane for comparison of absorption positions were made up to approximately 3×10^{-6} *M*. Absorption maxima found are shown in Table III. Fluorosulfonic acid was distilled and a few drops of SbF_5 added.

Table III

	Isooctane	Ethanol	Δ, cm^{-1}
Soret	25,202	25,361	+159
IV	20,161	20,117	−44
III	18,965	18,882	−56
II	17,559	17,615	+56
I	15,985	16,095	+110

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