

of known activation energies which are structurally analogous to those listed that have not been considered here, because of their slight differences from the ones given. The consistency of this theory is remarkable, considering that the same rule for estimating the parameters of the transition state gave agreement for the addition reactions of HX and X<sub>2</sub> to olefins and the exchange reactions between X<sub>2</sub> and H<sub>2</sub>.

An ambiguity exists in the interpretation of the kinetics of hydrogenation of 2,4-cyclopentadiene. The addition of molecular H<sub>2</sub> across either the 1,2 or 1,4 positions leads to the same product. The 1,4 type of elimination of molecular H<sub>2</sub> has been observed for 2,4-dihydrofuran,<sup>12</sup> while direct H<sub>2</sub> elimination from 2,3-dihydrofuran has never been observed. In our calculations it was assumed that the molecular H<sub>2</sub> added across the 1,2 position of cyclopentadiene. Excellent agreement between the calculated and the observed activation energy of hydrogenation of cyclopentadiene was found. The stepwise heats of hydrogenation of cyclopentadiene to 2-cyclopentene to cyclopentane are 24.0 and 26.9 kcal./mole, respectively,<sup>13</sup> indicating a near equivalence of the double bonds. This situation does not exist for furan, where the heat of hydrogenation of the first step is apparently

(12) C. A. Wellington and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 4888 (1961).

(13) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, *ibid.*, **59**, 831 (1937); G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *ibid.*, **58**, 146 (1936).

one-third the heat of the second step. While it would appear that the H<sub>2</sub> is adding 1,2 to cyclopentadiene, further investigation of the difference in the transition states of the two hydrogenation paths is now in progress.

## V. Ionic States in Olefin Chemistry

One of the very interesting aspects of the present calculation is the astonishingly low energies required to produce semi-ion pair states in the olefins. From Tables III, V, and VI we see that only 14.5 kcal. is required to produce a semi-ion pair in C<sub>2</sub>H<sub>4</sub> while half of this, only 7.5 kcal., is needed to do the same in *i*-C<sub>4</sub>H<sub>8</sub>. These energies are the least subject to error of all of the quantities that we have calculated and do not depend in any way on the model or the oversimplification of the charge density distribution. It seems to us that these low polarization energies must be intimately connected with the important kinetics of nucleophilic and electrophilic reactions at double bonds. They are also an indication that the ground states of olefins may already contain an important fraction of "ionic" character. In the aromatic family we believe that this can be demonstrated. We also believe that the *meta-ortho-para* directing effect of substituents in aromatic rings is a direct stabilization of the relevant semi-ion pair state by electrostatic polarization. In this sense it is closely related to the Markovnikov rule observed for the olefins. We hope to deal with this further in a future publication.

## Magneto-optical Rotation Spectra of Porphyrins and Phthalocyanines

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*Contribution from the Engineering Physics Laboratory, Experimental Station, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware. Received April 15, 1965*

*The magneto-optical rotation (m.o.r.) spectra of a number of porphyrins, phthalocyanines, and their metal derivatives were determined in an effort to correlate m.o.r. spectra with absorption spectra. Of the compounds studied, zinc and magnesium phthalocyanine had the largest magnetic rotations:  $-8 \times 10^5$  and  $-8.8 \times 10^5$ , respectively. No evidence could be obtained for relationships between the shape or the magnitude of the observed magnetic rotations and the ground-state para- or diamagnetism of the molecules. Some evidence was obtained for a relation between the shape of the m.o.r. spectrum and the polarizations of transitions in the absorption spectra. A description is given of an automatic recording m.o.r. spectropolarimeter with a solvent-compensating feature and a sensitivity of  $\pm 0.001$  and  $\pm 0.003^\circ$  for the visible and ultraviolet regions, respectively, of the spectrum.*

(1) Neurosciences Research Program, Massachusetts Institute of Technology, Brookline, Mass.

## Introduction

A study of the magneto-optical rotation (m.o.r.) spectra<sup>2</sup> of a number of porphyrins, phthalocyanines, and their metal derivatives was carried out in an effort to obtain experimental evidence for relationships of m.o.r. to absorption spectra. The porphyrins and phthalocyanines as a group are very suitable for such investigations since they have the largest magnetic rotations observed to date and are well characterized spectroscopically.<sup>3</sup>

In magneto-optical rotation spectroscopy, a magnetic field is used to induce an optical rotation (Faraday effect) in a molecule. The variation of this magnetically induced optical rotation with wave length gives an "m.o.r. spectrum." In a previous paper,<sup>4</sup> five general

(2) V. E. Shashoua, *J. Am. Chem. Soc.*, **82**, 5505 (1960).

(3) (a) M. Gouterman, *J. Mol. Spectry.*, **6**, 138 (1961); (b) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964.

(4) V. E. Shashoua, *J. Am. Chem. Soc.*, **86**, 2109 (1964).

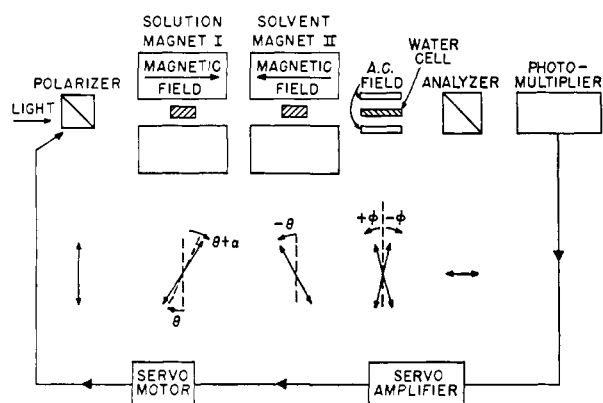


Figure 1. Diagram of m.o.r. spectropolarimeter illustrating operation of the instrument:  $\theta$ , solvent rotation;  $\alpha$ , solute rotation; and  $\phi$ , modulation angle in Faraday coil.

types of m.o.r. spectra were reported for several molecules at their optical absorption band regions (see Figure 2). This classification is again used in this paper to describe the m.o.r. results for a number of porphyrins and phthalocyanines in the long wave length absorption region of the molecules.

### Experimental

**Apparatus and Method of Measurement.** Figure 1 is a diagram of the instrument constructed at this laboratory for the measurement of m.o.r. spectra. The induced magnetic rotation of plane polarized light (Faraday effect) is measured as a function of wave length with an angular sensitivity of  $\pm 0.001$  and  $\pm 0.003^\circ$  for the visible and ultraviolet spectral regions, respectively. This apparatus has a solvent-compensating feature which permits direct measurement of solute rotation. It represents a large improvement over our previously described instrument<sup>4</sup> in rapidity of determination of m.o.r. spectra. The design details will be described elsewhere.<sup>5</sup> Basically, in the operation of the instrument, the plane-polarized light beam (see Figure 1) is rotated by an angle  $+\theta + \alpha$  after passing through the sample in the first 5000-gauss magnetic field and rotated by an angle of  $-\theta$  in the second 5000-gauss magnetic field. Since the magnetic fields are polarized in opposite directions, a net rotation of  $\alpha$  is obtained for the solute under investigation. An a.c. magnetic field<sup>6</sup> is used in the same manner as in Trageser's equipment to modulate the light beam by inducing Faraday rotations in a sample of water (20 cm. long). This provides a carrier frequency to activate the angle-sensing and recording sections of the apparatus. A 150-w. d.c. xenon arc is used as the light source, and a Cary Model 14 double-beam monochromator provides wave length selection. The sample temperature is kept constant to within  $0.1^\circ$ .

The results reported in this paper are expressed as a plot of specific magnetic rotation, defined by eq. 1, as a function of wave length. The data are normalized to a standard 10,000-gauss magnetic field.  $\theta$  is the angle

$$[\alpha]_{sp} = \frac{\theta}{lc} \left( \frac{10,000}{H} \right) \quad (1)$$

(5) J. G. Forsythe, R. Kieselbach, D. J. Troy, and V. E. Shashoua, *J. Appl. Opt.*, in press.

(6) M. B. Trageser, *J. Opt. Soc. Am.*, **42**, 866 (1952).

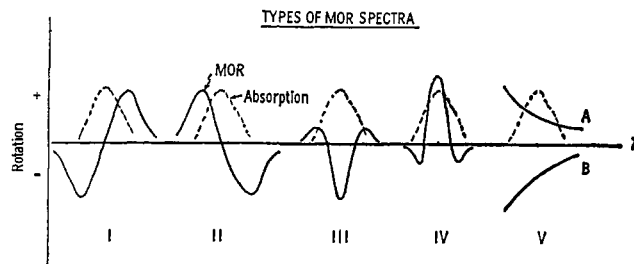


Figure 2. General types of m.o.r. spectra.

of rotation in degrees,  $l$  is the path length in decimeters,  $c$  is the concentration in g./ml., and  $H$  is the magnetic field in gauss. This apparatus has one disadvantage over the single magnetic field instrument in that it is not possible to compensate easily for the quantity of solvent displaced by the dissolved solute. This, however, can usually be neglected when the concentrations of solute are below 0.1%. The monochromator band pass was kept below one-tenth of half the band width under investigation to avoid spurious slit-width effects which arise from large band-pass measurements.

**Materials.** N-Methylpyrrolidone and chloronaphthalene were purified by vacuum distillation before use as solvents. Hematoporphyrin was obtained from Nutritional Biochemicals Corp. and used without further purification. Zinc hematoporphyrin was synthesized by heating a solution of hematoporphyrin in N-methylpyrrolidone with a 5:1 mole excess of zinc acetate at  $50^\circ$  for 2 hr. The absorption spectrum of the product was used to determine the formation of the product. Coproporphyrin was a preparation of Dr. I. T. Kay, Department of Medicine, University of Minnesota, obtained from Dr. P. J. McCartin (Du Pont Co.).

Phthalocyanine and its metal derivatives were all commercial products. The copper and nickel phthalocyanine derivatives were purified samples prepared by Dr. G. Sloan (Central Research Department, E. I. du Pont de Nemours & Co., Inc.) by sublimation at  $500^\circ$  under nitrogen.

### Results and Discussion

Table I and Figures 3 to 9 summarize the m.o.r. spectral results for the phthalocyanines and porphyrins studied. For each compound, the absorption spectrum is included in the figure for the same concentration used in the m.o.r. measurement. For coproporphyrin and hematoporphyrin, the natural optical activity of the compounds was also determined to give the optical rotatory dispersion (O.R.D.) spectra. Both the porphyrin and phthalocyanine data show large specific magnetic rotations with several anomalous dispersion features in the m.o.r. spectra at absorption bands. For example, zinc phthalocyanine and magnesium phthalocyanine have the largest magnetic rotation observed to date, *i.e.*,  $-8.3 \times 10^5$  and  $-8.8 \times 10^5$  at their 670- and 675-m $\mu$  absorption bands, respectively.

**Relationship of M.o.r. Spectra to Absorption Spectra.** In a discussion of the absorption spectra of porphyrins, Gouterman and Stryer<sup>7,8</sup> point out that theoretical

(7) M. Gouterman and L. Stryer, *J. Chem. Phys.*, **37**, 2260 (1962).

(8) M. Gouterman, *ibid.*, **33**, 1523 (1960).

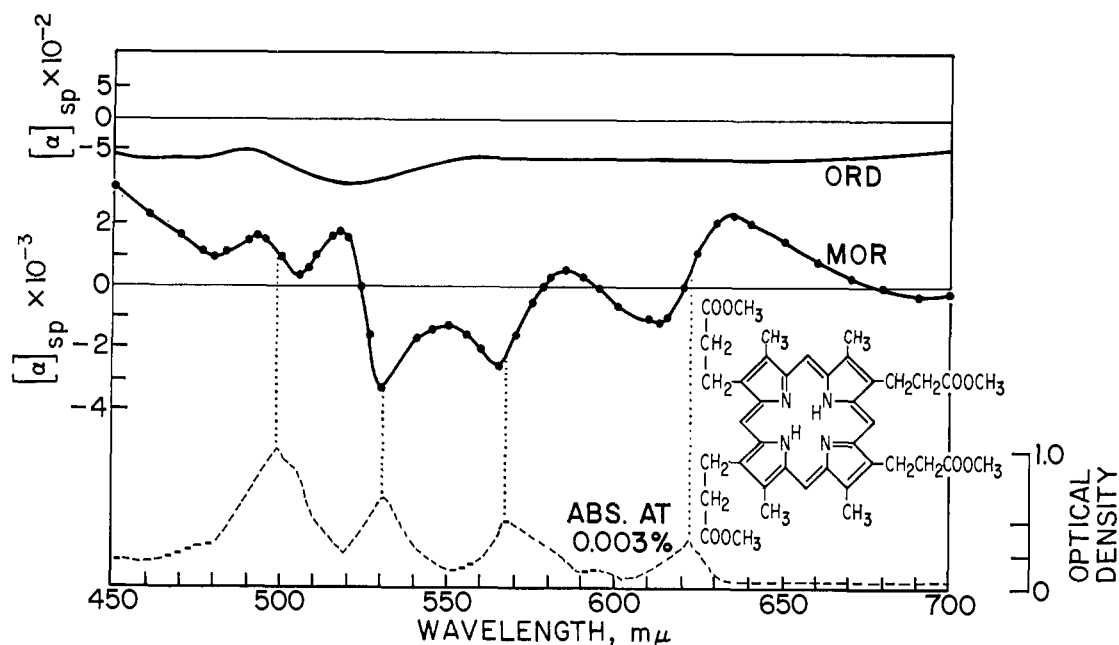


Figure 3. M.o.r. and o.r.d. spectra of coproporphyrin-II (tetramethyl ester) in N-methylpyrrolidone.

considerations, such as those developed by Simpson,<sup>9</sup> Platt,<sup>10</sup> and Gouterman,<sup>11</sup> indicate that the spectra at the long wavelength absorption region arise from  $\pi \rightarrow \pi^*$  transitions. Furthermore, the  $D_{2h}$  symmetry of the free base porphyrins indicates two axes of symmetry in the plane of the ring system. The four ab-

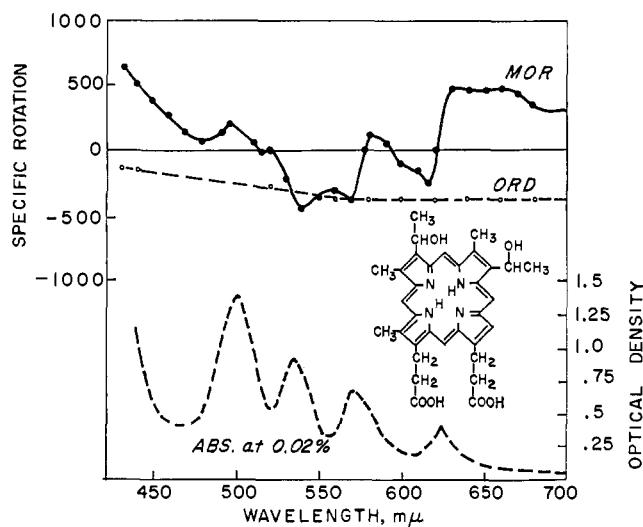


Figure 4. M.o.r. and o.r.d. spectra of hematoporphyrin in N-methylpyrrolidone.

sorption bands (see Figure 3) in the visible region are classified as  $Q_x(0 \leftarrow 0)$ ,  $Q_x(1 \leftarrow 0)$ ,  $Q_y(0 \leftarrow 0)$ , and  $Q_y(1 \leftarrow 0)$ , where  $x$  and  $y$  represent axes parallel and perpendicular to the central hydrogen atoms of the molecule and indicate the direction of polarization of the transitions. Experimental verification of these postulates was obtained from fluorescence studies.<sup>7</sup>

(9) W. T. Simpson, *J. Chem. Phys.*, **17**, 1218 (1949).

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

(11) M. Gouterman, *J. Chem. Phys.*, **30**, 1139 (1959).

An analysis of the m.o.r. spectrum of coproporphyrin II tetramethyl ester (Figure 3) in these terms gives a curious relationship of the shape, or type, of m.o.r.

Table I. M.o.r. Spectral Data for Porphyrins and Phthalocyanines

Compound	Solvent <sup>a</sup>	$\lambda$ , m $\mu$	$[\alpha]_{sp}^b$	Type <sup>c</sup>
Coproporphyrin-II (tetramethyl ester)	NMP	622 (-)	$3.6 \times 10^3$	I
		518 (-)	$2.6 \times 10^3$	I
		530 (-)	$3.3 \times 10^3$	II
		498 (+)	$1.4 \times 10^3$	II
Hematoporphyrin	NMP	624 (-)	700	I
		570 (-)	350	I
		535 (-)	420	II
		500 (+)	220	II
Zinc hematoporphyrin	NMP	578 -	$4.4 \times 10^4$	III
		-	$1.1 \times 10^4$ <sup>e</sup>	III
		538 -	$1.35 \times 10^4$	III
Phthalocyanine	CIN	698 (-)	$150 \times 10^4$	I
		662 -	$66 \times 10^4$	II (?)
		635 -	$15 \times 10^4$	III
		602 (+)	$7.5 \times 10^4$	II
Copper phthalocyanine	NMP	670 -	$21 \times 10^4$	III
		638 -	$0.9 \times 10^4$	III
		608 (-)	$1.9 \times 10^4$	II
		670 -	$83 \times 10^4$	III
Magnesium phthalocyanine	NMP	640 -	$5 \times 10^4$	III
		605 (-)	$8.5 \times 10^4$	II
		671 -	$88 \times 10^4$	III
		640 -	$5 \times 10^4$	III
Zinc phthalocyanine	NMP	605 (-)	$8.2 \times 10^4$	II
		670 (-)	$66 \times 10^4$ <sup>d</sup>	III
		670 (-)	$66 \times 10^4$ <sup>d</sup>	III

<sup>a</sup> NMP, N-methylpyrrolidone, CIN, chloronaphthalene. <sup>b</sup> (+) and (-) represent the sign of the magnetic rotation at the inflection points of the types-I and -II m.o.r. spectra. <sup>c</sup> See Figure 2 for definitions of m.o.r. spectral types. <sup>d</sup> Owing to the extreme insolubility of the compound, this result was estimated by considering that the extinction coefficient for the 670-m $\mu$  band was about the same as for magnesium phthalocyanine. <sup>e</sup> M.o.r. bands associated with the 540 m $\mu$  absorption (see Figure 5).

spectrum (see Figure 2) to the polarization of the transition. In Figure 3, the coproporphyrin data show that the  $Q_x(0 \leftarrow 0)$  band at 622 m $\mu$  has a type I m.o.r.

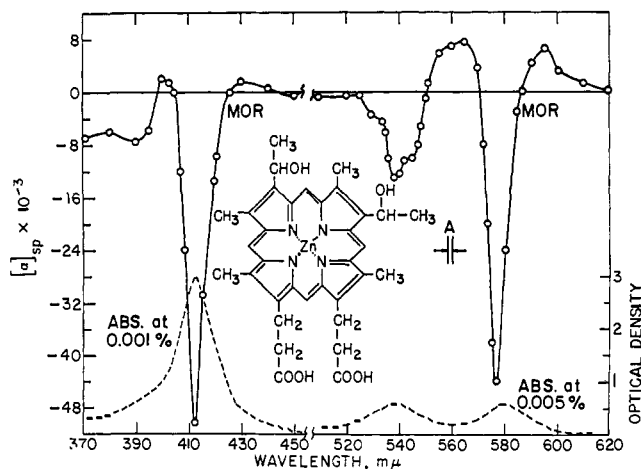


Figure 5. M.o.r. spectrum of zinc hemtoporphyrin in N-methylpyrrolidone (A, monochromator band pass).

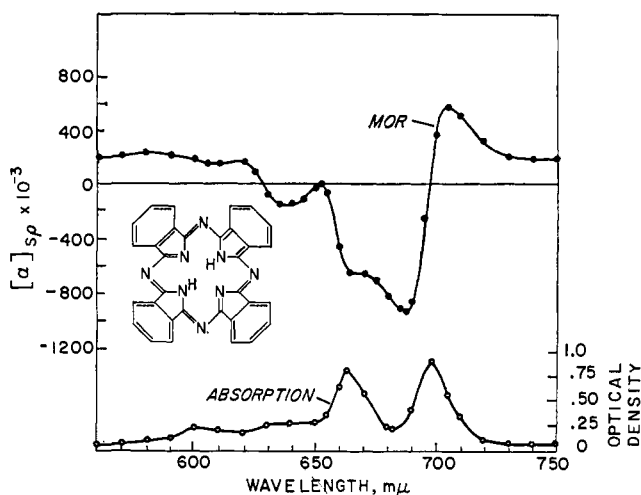


Figure 6. M.o.r. spectrum of phthalocyanine in 2-chloronaphthalene (monochromator band pass = 1.5 mμ).

spectrum. The absorption peak at the 568-mμ  $Q_x(1 \leftarrow 0)$  band, however, coincides with a negative m.o.r. peak suggesting that this may be a type-III m.o.r. spectrum. However, an m.o.r. positive peak at 580 mμ is difficult to explain since the absorption does not peak at that wave length. If we assume that  $Q_x(1 \leftarrow 0)$  is centered at 572 mμ, rather than 568 mμ, then both the  $Q_x(0 \leftarrow 0)$  and  $Q_x(1 \leftarrow 0)$  would have type I m.o.r. spectra. Similarly, the 530-mμ  $Q_y(0 \leftarrow 0)$  band coincides with a negative m.o.r. peak, but if we assume that the absorption band is centered at 525 mμ, then the m.o.r. spectrum becomes a type II, and it becomes easy to account for the positive m.o.r. peak at 514 mμ as the positive lobe of the sigmoid-shaped type-II m.o.r. spectrum. The 500-mμ absorption band,  $Q_3(1 \leftarrow 0)$ , also has a type-II m.o.r. spectrum. If these assumptions are valid, then the shape of an m.o.r. spectrum would contain some parameter related to the polarization of a transition. In Figure 4 this same type of considerations seems to be applicable to the hemtoporphyrin m.o.r. data, even though unsymmetrical substituents disrupt the unique  $x$  and  $y$  axes of the molecule. The 4- to 5-mμ shifts in the absorption band maxima of these compounds required for the above assumptions are quite reasonable especially since the

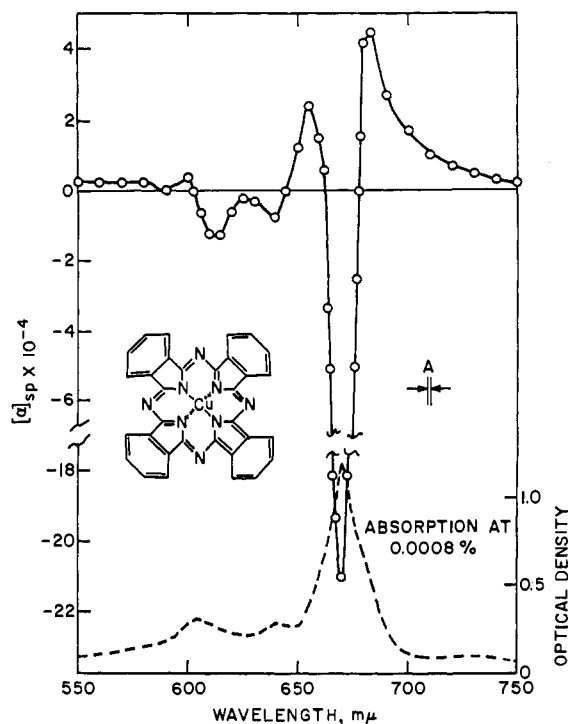


Figure 7. M.o.r. spectrum of copper phthalocyanine in N-methylpyrrolidone (A, monochromator band pass).

( $0 \leftarrow 1$ ) $_{x,y}$  bands may be complex mixtures of  $x$  and  $y$  polarizations of several vibrational bands as observed by Rimington, Mason, and Kennard<sup>12</sup> for a related compound (porphin). One piece of additional evidence for this may be obtained by considering the spectrum of zinc hemtoporphyrin in Figure 5. Here, the m.o.r. spectrum (Figure 5) shows a negative peak (type III) with no apparent difference in polarization between the two bands at 538 and 578 mμ. There is, however, a suggestion of vibrational structure for the 538-mμ band, which may be produced by the effect of unsymmetric substitution to disturb the unique  $x$  and  $y$  polarizations of the ring. These results suggest an analogy to Solevi'er's<sup>13</sup> polarized fluorescence studies on zinc porphyrin where  $Q_x$  and  $Q_y$  are degenerate and the bands behave as planar oscillators with emission and absorption occurring in a single plane.

Another observation about the relationship of m.o.r. spectra to the absorption measurements is illustrated by comparing the magnetic rotational strengths (Figure 5) as measured by the specific magnetic rotation, for the 410- and the 578-mμ bands of zinc hemtoporphyrin. Here, essentially the same specific magnetic rotation ( $-4.8 \times 10^4$ ) is obtained for two absorption bands in the same molecule which differ in intensity by a factor of about 15. This and the previous data on potassium ferricyanide<sup>4</sup> provide a good verification for Tinoco and Bush's<sup>14</sup> suggestion that the magnetic rotation should bear no relation to the intensity of an absorption band; *i.e.*, weak absorption bands may have strong magnetic rotations and strong absorption bands may have weak magnetic rotational strength, and *vice versa*.

(12) C. Rimington, S. F. Mason, and O. Kennard, *Spectrochim. Acta*, **12**, 65 (1958).

(13) K. N. Solevi'er, *Opt. Spectry.* (USSR), **10**, 389 (1961).

(14) I. Tinoco, Jr., and C. A. Bush, *Biophysics Symp.*, **1**, 209 (1964).

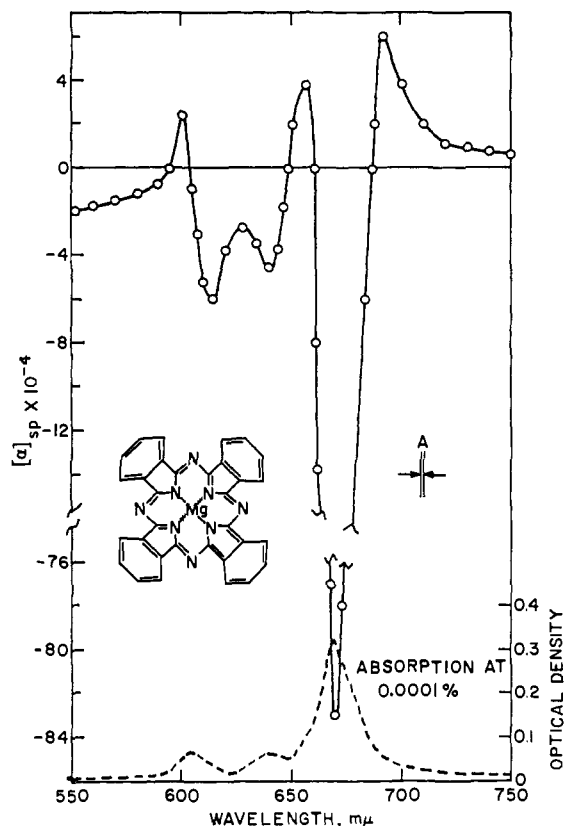


Figure 8. M.o.r. spectrum of magnesium phthalocyanine in N-methylpyrrolidone (A, monochromator band pass).

*Relationship of M.o.r. Spectra to Paramagnetism.* Earlier studies of the Faraday effect<sup>15</sup> have suggested a relationship of the para- or diamagnetism of a molecule to the shape and magnetic rotational strength of an m.o.r. spectrum. The results on phthalocyanine (Figures 7-9) and its various metal derivatives show that this type of consideration cannot be easily applied. In fact, copper phthalocyanine with a magnetic moment of 1.73<sup>16</sup> has about the same specific magnetic rotation for its 670-m $\mu$  band ( $-2.1 \times 10^5$ ) as the diamagnetic nickel phthalocyanine<sup>17</sup> ( $-6.6 \times 10^5$ ). Moreover, both these substances and the magnesium and zinc phthalocyanines (Figures 8 and 9) have type-III m.o.r. spectra at their 670-m $\mu$  band absorption region, indicating that there is no obvious relationship of the ground-state paramagnetism or diamagnetism of a compound to the shape or the rotational strength of its m.o.r. spectrum.

(15) For a comprehensive review see: J. R. Partington, "Advanced Treatise on Physical Chemistry," Vol. IV, Longmans, Green and Co., London, 1954, pp. 592-632.

(16) R. Haremann, W. Haberditzl, and K. H. Mader, *Z. physik. Chem. (Leipzig)*, 218, 71 (1961).

(17) H. Senff and W. Klemm, *J. prakt. Chem.*, 154, 73 (1939).

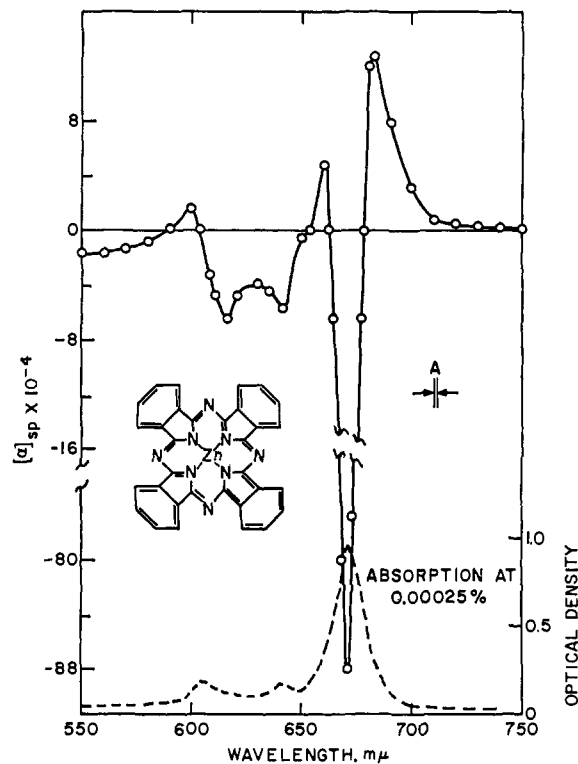


Figure 9. M.o.r. spectrum of zinc phthalocyanine in N-methylpyrrolidone (A, monochromator band pass).

*Significance of Results.* The results of this paper point to three possible generalities about m.o.r. spectroscopy:

(1) The m.o.r. spectrum at the absorption band region of a molecule, as shown by the zinc hematoporphyrin (see Figure 5) and potassium ferricyanide<sup>4</sup> data, is related to some additional parameter than merely its ability to absorb light. This parameter influences the magnetic rotational strength of a molecule.

(2) The shape of an m.o.r. spectrum, as shown by the coporphyrin and hematoporphyrin (Figures 4 and 5) data, appears to be related to the polarization of a transition.

(3) The para- or diamagnetism of the ground state of a molecule appears to bear no obvious relationship to the shape or magnetic rotational strength of a substance.

*Acknowledgment.* It is a pleasure to thank Messrs. J. G. Forsythe, R. Kieselbach, and D. J. Troy of the Engineering Physics Laboratory for their valuable assistance in the construction of the m.o.r. spectropolarimeter, and Dr. P. J. McCartin of Radiation Physics Laboratory of the Du Pont Company for stimulating discussions.