# Magnetic Circular Dichroism and Absorption Spectra of the Porphyrins. Part I

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We have measured the magnetic circular dichroism and absorption spectra of free base porphyrin, mono- and di-acid forms and a number of metalloporphyrins. Three of these, free base octaethylporphyrin, zinc and copper octaethylporphyrins have been studied in rigid media at liquid helium temperatures, the remainder as solutions at room temperature. From studying the protonated forms we find no support for the $n \longrightarrow \pi^*$ interpretation of Corwin. The remaining spectra fit reasonably well with established theory in that the metal is only weakly coupled to the ring $\pi$ system and takes little part in the optical transitions in the metalloporphyrins studied in this work. Close examination of the bandwidths of the free base spectra at low temperatures suggests an underlying weak transition which may be $n \longrightarrow \pi^*$ in character. Much vibronic structure is observed at low temperature in the $Q_1$ band and it is clear that several vibronic states are excited which accounts for the observation by Anex of mixed polarisation in the second band. Using the functions of Gouterman we obtain some justification for the experimental observation that the $Q$ bands are split much more than is the Soret band on going from metalloporphyrin to free base.

THEORIES of the electronic structure and spectra of the porphyrins[1] have the characteristic that they are conceptually very simple for such complex molecules. Yet despite this simplicity the theory is capable of explaining most of the properties of the optical electrons and only the more subtle features, *e.g.* band widths, low-symmetry splittings, and absolute intensities do not easily fit into the pattern. In the usual approach the role of the central metal ion in the metalloporphyrins is a relatively minor one[2] in most cases. Except in one or two special instances, namely $Fe^{II}$, $Fe^{III}$, and $Mn^{III}$, the metal orbitals are considered to be only very weakly coupled to those of the porphyrin ring and are not involved in the excitations of the optical electrons. The metal essentially ensures that the symmetry of the ring system is $D_{4h}$. In the absence of the metal, the free base porphyrin has symmetry $D_{2h}$. Thus removal of the metal and the addition of two protons is equivalent to a perturbation of the ring system which has $D_{2h}$ symmetry and which splits the degenerate states of the metalloporphyrin. This relative invariance to the nature of the metal does not parallel the biological significance of the central metal ion where its precise nature is of crucial importance in the function of chlorophyll, the cytochromes, haemoglobin, and myoglobin for example. If this is the case then one might predict that the absorption spectra would give relatively little information which can be directly related to the biological function of the metal.

In order to investigate this aspect of the theory more thoroughly we have examined the magnetic circular dichroism (m.c.d.) and absorption spectra of some porphyrins very carefully including measurements in rigid media at low temperatures. We have chosen for this study a series of highly symmetric porphyrins namely octaethylporphyrin (OEP) (Figure 1a) and its metal derivatives and our spectra are of free base, $Cu^{II}$, $Zn^{II}$, $Co^{II}$, and $Ag^{II}$ octaethylporphyrins. The first three of these were studied at liquid-helium temperatures, the remainder as solutions at room temperature. Our results largely confirm the accepted picture of the electronic structure and though a number of new features emerge from the low-temperature spectra, our conclusion is that for the metals we have studied the absorption and m.c.d. spectra are rather little influenced by the nature of the central metal, and that the metal orbitals are not strongly involved in the optical transi-

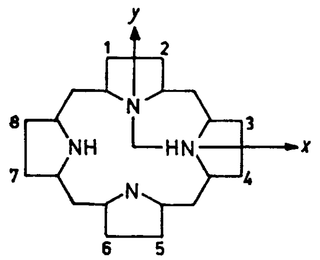

FIGURE 1 The basic porphin skeleton. (a) For octaethylporphyrin, 1—8 = Et. (b) For mesoporphyrin IX, 1,3,6 and 7 = Me, 2,8 = Et, 4 and 5 = $CH_2CH_2COOCH_3$

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[1] M. Gouterman, *J. Mol. Spectroscopy*, 1961, **6**, 138.

[2] M. Gouterman, *J. Chem. Phys.*, 1959, **30**, 1139.

tions. This is not the case however with the $Fe^{II}$, $Fe^{III}$, and $Mn^{III}$ porphyrins where charge-transfer transitions are seen and these will be the subject of a further communication.

One other point of interest is discussed in this work and definitive evidence obtained. It has been suggested recently[3] from a study of the spectral changes of porphyrins on acidification, that the visible bands are due to $n \longrightarrow \pi^*$ transitions of the nitrogen atoms. To test this we have run the m.c.d. spectra of the mono- and di-acid forms of mesoporphyrin IX (Figure 1b) and our results do not justify this interpretation.

## EXPERIMENTAL

All samples of free base and metalloporphyrins were very generously provided by Professor A. W. Johnson and Dr. P. Batten. Solution m.c.d. and absorption spectra were run in dichloromethane. Absorption spectra were measured on a Cary 14 and the m.c.d. spectra on a JASCO ORD/UV5 fitted with an Oxford Instruments superconducting magnet with fields up to 5·0 T. We also ran m.c.d. spectra on an instrument built at the National Physical Laboratories and currently on loan to the authors. This latter instrument has sensitivity some two orders of magnitude greater than the JASCO instrument and we were able to use a 0·33 T permanent magnet to obtain m.c.d. spectra. For low-temperature work the porphyrins were dissolved in methylmethacrylate which was then polymerised using azobisisobutyronitrile or atmospheric oxygen as an initiator. The samples were then cut to size and the faces polished for optical examination. Room-temperature m.c.d. and absorption spectra of porphyrins in the polymer were identical to those obtained in dichloromethane. Low-temperature spectra were obtained by mounting the samples in the helium bore of the superconducting magnet.

The spectra of mesoporphyrin IX were obtained by dissolving a similar weight of substance in acetone (10 ml), acetic acid–acetone (10 ml, 60 : 40), and α-bromopropionic acid–acetone (10 ml, 60 : 40) for the free base, monoacid, and diacid forms respectively.

The $A/D$ and $B/D$ values were computed by taking moments about the band centre defined to make $\langle\varepsilon\rangle_1 = 0$. The accuracy of these values is limited by the usual problems of working with very small quantities of sample and the possibility in the free base spectra particularly of contamination by trace quantities of metal. Where possible we have checked our spectra against previously published data and we find these to be in agreement.

## DISCUSSION

An outline of the currently accepted theory of electronic structure of porphyrins is as follows. Simple LCAO-MO theory[4] is used to construct the molecular orbitals for the porphyrin π-electron system. This gives two highest occupied MO's having $a_{1u}$ and $a_{2u}$ symmetry and a doubly degenerate lowest unoccupied orbital having $e_g$ symmetry (Figure 2). Two simple one-electron $\pi \longrightarrow \pi$ transitions can then take place, $a_{1u} \longrightarrow e_g$ and $a_{2u} \longrightarrow e_g$. That is, we have a ground state $a_{1u}^2\, a_{2u}^2\rangle$, $^1A_{1g}$, and two excited states $|a_{1u}^2\, a_{2u}^1\, e_g^1\rangle$, $^1E_u^{(1)}$, and $|a_{1u}^1\, a_{2u}\, ^2e_g^1\rangle\ ^1E_u^{(2)}$, both of which are doubly degenerate. With these excited states MO theory predicts two intense $\pi \longrightarrow \pi$ transitions and experimentally the porphyrins are found to have bands in the visible and near u.v. which could correspond to these excitations. However, the intensities are in the ratio of around 10 : 1 and to account for this the MO picture was refined by Gouterman[2] by the inclusion of configuration interaction between these two excited configurations. If states diagonal in first-order configuration interaction are formed, a difference in dipole strength of the two transitions is observed and this is the degree of sophistication of model which is in most general use. It is sometimes referred to as the four-orbital model.

| | | $Q_0$ | | $Q_1$ | | Soret | |
|---|---|---|---|---|---|---|---|
| Compound | $T$/K | Transition frequency (cm$^{-1}$) | $A/D$ ($\beta$) | Transition frequency (cm$^{-1}$) | $A/D$ ($\beta$) | Transition frequency (cm$^{-1}$) | $A/D$ ($\beta$) |
| Cu(OEP) | 300 | 17,780 | 1·73 | 18,890 | 0·59 | 24,920 | 0·19 |
| Cu(OEP) | 8 | 17,880 | 1·32 | 19,120 | 0·45 | 25,050 | 0·15 |
| Zn(OEP) | 300 | 17,540 | 1·77 | 18,710 | 0·9 | 24,840 | 0·15 |
| Zn(OEP) | 11 | 17,620 | 0·96 | Overlapping bands | | 24,670 | 0·13 |
| Ag(OEP) | 300 | 17,910 | 1·06 | 19,050 | 0·36 | 24,460 | 0·29 |
| Co(OEP) | 300 | 18,080 | 0·93 | 19,230 | 0·33 | 25,400 | −0·2 |
| Mesoporphyrin IX di acid | 300 | 16,740 | 0·51 | Overlapping bands | | 24,270 | 0·019 |

| | | $Q_{x0}$ | | $Q_{x1}$ | | $Q_{y0}$ | | $Q_{y1}$ | | Soret | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | $T$/K | Transition frequency (cm$^{-1}$) | $10^4B/D$ ($\beta$ cm) | Transition frequency (cm$^{-1}$) | $10^4B/D$ ($\beta$ cm) | Transition frequency (cm$^{-1}$) | $10^4B/D$ ($\beta$ cm) | Transition frequency (cm$^{-1}$) | $10^4B/D$ ($\beta$ cm) | Transition frequency (cm$^{-1}$) | $A/D$ ($\beta$) |
| OEP | 300 | 16,110 | −19 | 17,620 | −57 | 18,870 | 8·7 | 20,050 | 1·7 | 25,000 | 0·16 |
| OEP | 10 | 16,220 | −14 | 17,770 | −4·3 | 18,960 | 6·5 | Overlapping bands | | 25,130 | 0·10 |
| Mesoporphyrin IX | | | | | | | | | | | |
| free base | 300 | 16,120 | −17 | 17,650 | −11·9 | 18,930 | 16·3 | 20,160 | 2·03 | 25,350 | 0·19 |
| monoacid | 300 | 16,660 | −20·3 | Overlapping bands | | | | 18,830 | 2·07 | 25,540 | 0·0069 |

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[3] A. H. Corwin, A. B. Chivvis, R. W. Poor, D. G. Whitten, and E. W. Baker, *J. Amer. Chem. Soc.*, 1968, **90**, 6577.

[4] H. C. Longuet-Higgins, C. W. Rector, and J. W. Platt, *J. Chem. Phys.*, 1950, **18**, 1174.

The foregoing refers to porphyrins having $D_{4h}$ or approximate $D_{4h}$ symmetry such as the metalloporphyrins or the diacid form of the free base. These usually have spectra showing three bands in the visible and near u.v. as exemplified by the spectrum of Zn(OEP) (Figure 3). The two bands $Q_0$, $Q_1$ are the 0–0 and 0–1 vibronic components of the lowest energy transition ($Q$ in Figure 2) and the $B$ or Soret band is the $\pi \longrightarrow \pi^*$ excitation.

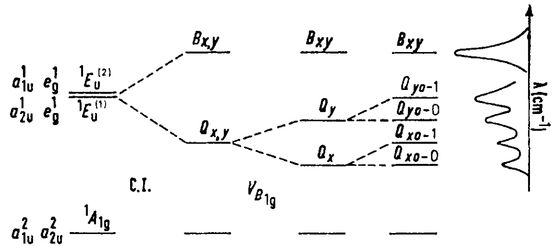

FIGURE 2 Energy-level diagram for first two electronic transitions. The simple one-electron configurations $E_u^{(1)}$, $E_u^{(2)}$ are split by configuration interaction (C.I.), to give $B$ and $Q$ states. In the $D_{2h}$ symmetry of free base porphyrin these are split into the components shown. The observed spectrum corresponds to transitions to the excited states shown where 0–0 refers to the electronic origin and 0–1 is the fundamental in some vibrational mode

A typical free base spectrum is shown in Figure 4. Now there are four bands in the visible and the $B$ band in the u.v. The interpretation of this spectrum is that the reduced symmetry of the free base, $D_{2h}$, causes tting of the degenerate $E_u$ states. In the $Q$ bands are well separated and are designated $Q_x$ and $Q_y$ for the two vibronic bands. This is clearly rather an unusual effect since the $Q$-band degeneracy is split by over 2500 cm$^{-1}$ in OEP yet the $B$ band is unsplit even at 6 K [though this band is very broad compared to the Soret bands in Cu(OEP) and Zn(OEP)]. This peculiarity has not been accounted for in the theory and is discussed in more detail later in this paper.

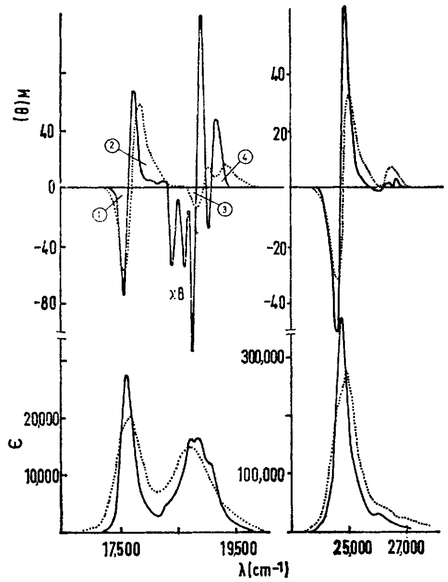

FIGURE 3 MCD and absorption spectra of Zn(OEP). Dashed curves are the room temperature spectra and the full curves at *ca.* 8 K both in poly(methyl methacrylate). $[\theta]_M$ is the ar ellipticity (defined as in natural optical activity in dl dm$^{-1}$ mol$^{-1}$). ε is the molar extinction coefficient

Explanations for the visible bands, other than that they are two vibronic components of a single electronic transition in the $D_{4h}$ molecule which are each split into two components in the free base, are possible. The emission spectra provide very strong evidence that the first two bands are vibronic lines of a single electronic transition since the emission spectrum is a mirror image of the first two bands with $Q_0$ as origin.[5] The m.c.d. spectra obtained from the m.o.r.d. data of Shashoua,[6] also provide strong evidence in favour of the MO interpretation.

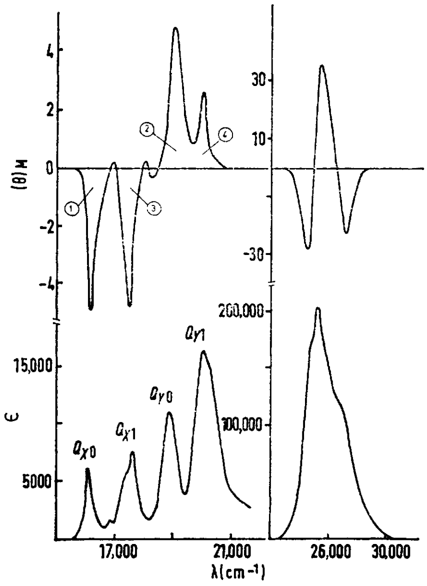

FIGURE 4 M.c.d. and absorption spectra of mesoporphyrin IX in dichloromethane at room temperature. $[\theta]_M$ and ε as in Figure 3

In a recent paper Corwin[3] has suggested that the visible bands are due to $n \longrightarrow \pi^*$ transitions of lone pairs on the tetrapyrrole nitrogen atoms. In this interpretation Corwin argues that there are four lone pairs, two ' pyrrole type ' and two ' pyridine type ' in the free base. Transitions from these four produce the four absorption bands of the free base. When the monoacid is formed a three-banded spectrum results (Figure 5) and the diacid gives two bands (Figure 6). This Corwin suggests is due to the successive protonation of the pyrrole-type lone pairs, leaving three and two non-bonding pairs in the mono- and di-acid respectively. This argument is very difficult to uphold.

Apart from the intensity question discussed by Corwin, namely that $n \longrightarrow \pi^*$ transitions are rarely found with

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. P. Gurinovich, A. N. Sevchenk, and K. N. Solev'ev, *and Spectroscopy*, 1961, **10**, 396.

[6] P. J. Stephens, W. Suetaka, and P. N. Schatz, *J. Chem. Phys.*, 1966, **44**, 4592.

extinction coefficients of 20—30,000 l mol$^{-1}$ cm$^{-1}$, there are two pieces of physical evidence which militate against the $n \longrightarrow \pi^*$ interpretation. The first is the two-banded emission spectrum [5] which is very strong evidence indeed that the first two bands in the free base and in the metalloporphyrin are transitions to the same electronic level. The second piece of evidence is the m.c.d. work of Schatz *et al.* which fits the established MO theory rather well. We have examined the m.c.d. of the mono- and di-acid forms of mesoporphyrin IX dimethyl ester (meso IX) and our conclusions do not support the $n \longrightarrow \pi^*$ interpretation.

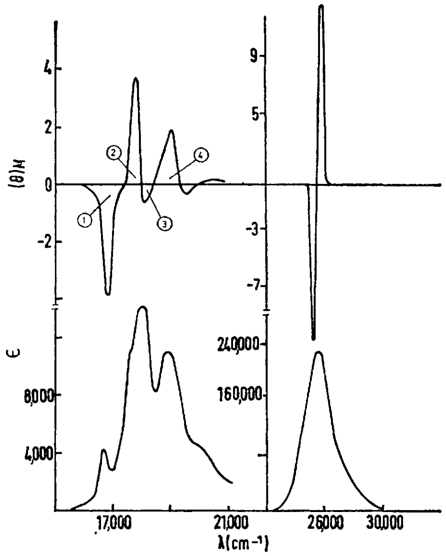

FIGURE 5 M.c.d. and absorption spectra of the monoacid of mesoporphyrin IX at room temperature. $[\theta]_M$ and $\epsilon$ are defined as in Figure 3

To illustrate this point let us consider the spectra of Zn(OEP), and the free base, the monoacid and the diacid of mesoporphyrin IX (Figures 3—6 respectively). The protonated forms were obtained using the method of Corwin and the spectra agree identically with his. Turning first to the zinc salt (Figure 3) we observe in the visible region two positive $A$ terms at room temperature, as noted by Schatz *et al.*[6] This is in agreement with the MO interpretation of a transition to a degenerate excited state $Q_0$, followed by one quantum of a totally symmetric vibration $Q_1$. We shall number the positive and negative regions of these $Q_0$, $Q_1$ $A$ terms as shown in Figure 3. In the free base these degeneracies are split by *ca.* 2600 cm$^{-1}$ and the location of the components is as shown in Figure 4. If the monoacid spectrum represents some other low-symmetry distortion of the basic two $A$-term spectrum we should expect to discern the four components as in the free base, but probably differently ordered since the splitting will not be the same. That this is the case can be seen in Figure 5 where the bands at 16,800 and 17,400 cm$^{-1}$ are components 1 and 2 of $Q_0$ and those at 18,000 and 18,600 cm$^{-1}$ are the components 3 and 4 of $Q_1$. These components are not as clear in the absorption spectrum, since two of the bands overlap quite strongly, but this gives an indication of the power of the m.c.d. spectrum in unravelling a complex situation of this type, since the four lobes are easily discerned. The four-component structure can also be seen in the diacid spectrum in Figure 6, and these are numbered in the drawing. Both this and the monoacid spectrum are explicable on the basis of the MO model but cannot be accounted for in the $n \longrightarrow \pi^*$ interpretation.

The free base, mono- and di-acid spectra give, on closer inspection, some insight into the situation of the protons in the centre of the porphyrin ring. Thus on going from metalloporphyrin to free base the degenerate $Q$-vibronic states are split by 2500 cm$^{-1}$ which indicates a considerable interaction between the pyrrole hydrogens leading to a fairly strong perturbation of $D_{2h}$ symmetry. In the monoacid however, the low-symmetry ($C_{2v}$) distortion produces a different splitting pattern of much smaller magnitude. The first effect might be expected since the distortion has a different symmetry, but the reduced magnitude is rather surprising and suggests that the strain in the tetrapyrrole ring is relieved by distortion of the hydrogens out of plane in the monoacid. This is more marked in the diacid where the distortion is less than the bandwidth (*ca.* 700 cm$^{-1}$) in magnitude and some low-energy arrangement of the four hydrogens must result. This presumably is a staggered two up and two down ordering which technically destroys the $D_{4h}$ symmetry of the molecule, but which does not alter the symmetry of the $\pi$ electrons and orbitals which comprise the optical electronic system.

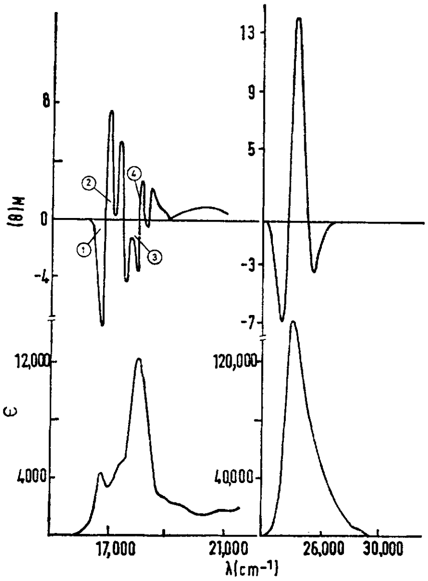

FIGURE 6 M.c.d. and absorption spectra of the diacid of mesoporphyrin IX at room temperature. $[\theta]_M$ and $\epsilon$ are defined as in Figure 3

The diacid spectrum shows some unusual features together with the two $A$-term m.c.d. Shoulders in the absorption at 17,400 and 18,200 cm$^{-1}$ are associated with negative and positive $A$ terms respectively. The first of these is exceptional in that negative $A$ terms have not been found in the $Q$ bands of other porphyrins. This could arise from four sources. Firstly it could be a trace-metal impurity introduced by the acid. This seems unlikely since none of the metalloporphyrins we have studied shows an $A$ term of this sign. A second possibility is that these two bands are the $n \longrightarrow \pi^*$ transitions. However this can be ruled out since the bands do not appear in the free base nor the monoacid spectra. Thirdly they could be due to isomers, *cis*- and *trans*-forms of the four central hydrogens. This again is unlikely since a perturbation so small that no appreciable splitting is discerned could scarcely completely reverse the sign of the $Q$-band m.c.d. Finally, the most likely explanation which is that these two, together with the $Q_1$ band, are vibrational components of the electronic $A_{1g} \longrightarrow Q_0$ transition. The m.c.d. spectra are those of the vibronic states and thus reflect the magnetic moments of the excited vibronic states. $Q_1$ is one quantum of a totally symmetric vibration built on the electronic origin $Q_0$, and thus will be the same sign (and have the same magnitude $A/D$) as $Q_0$. Molecular vibrations exist which will give vibronic states having $A$ terms of opposite sign to the origin and we suggest that the band at 17,400 cm$^{-1}$ is a fundamental in one of these. The second $A$ term at 18,200 cm$^{-1}$ may then be the first overtone in this mode since 0–2 would have $a_{1g}$ symmetry giving again a positive $A$ term. This fits reasonably well with the separations from $Q_0$. Alternatively the second band may represent another fundamental in a different normal mode.

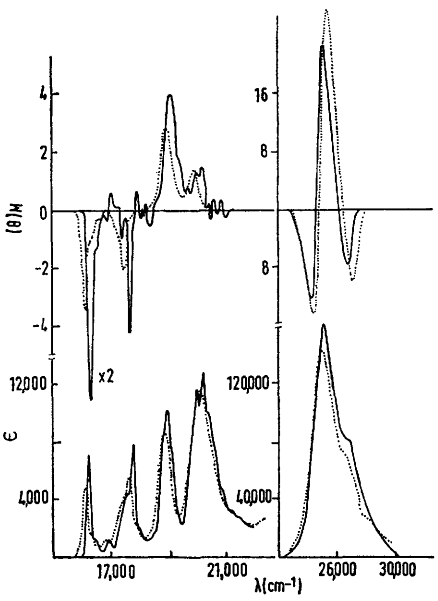

FIGURE 7 M.c.d. and absorption spectra of octaethylporphyrin. Dotted curves, room temperature; full curves, *ca.* 8 K; both in polymethylmethacrylate. $[\theta]_M$ and $\varepsilon$ are defined as in Figure 3

The m.c.d.s of the Soret region are perplexing. That of Zn(OEP) is straightforward with the $A$ term expected for $^1A_{1g} \longrightarrow {}^1E_u$. In the free base this appears to become two overlapping $A$ terms of opposite sign. This will be discussed a little later but in the monoacid the Soret region is again a single, sharp, structureless $A$ term. In the diacid the two overlapping $A$-term shape returns. This seems to illustrate the principle that the splittings of one state are not related to those of another in a molecule despite the states having the same symmetry. We develop this point further later in the paper.

Having discussed the evidence against the $n \longrightarrow \pi^*$ interpretation, we now turn to the question of the role of the metal ion in the metalloporphyrins. With this aim we have examined a series of metalloporphyrins which are both paramagnetic and diamagnetic. Two of these, Zn(OEP) and Cu(OEP) together with the free base have been incorporated into a rigid matrix and their absorption and m.c.d. spectra measured at liquid-helium temperatures. These spectra at room and low temperatures are shown in Figures 3 and 7—9. As can be seen from the spectra, the gross overall picture of absorption and m.c.d. does not change in any appreciable way with metal. Thus in the low-temperature spectra of Zn(OEP) and Cu(OEP) we can pick out $Q_0$ and $Q_1$ and the Soret band clearly with their positive $A$ terms. Differences are found, however; thus, $Q_0$ in Zn(OEP) is at 17,600 cm$^{-1}$ and in Cu(OEP) at 17,850 cm$^{-1}$ and there is a shift of similar magnitude in the Soret band. This has been interpreted by Williams[7] in terms of the electron-acceptor properties of the cation and by Gouterman[2,8] in terms of an inductive

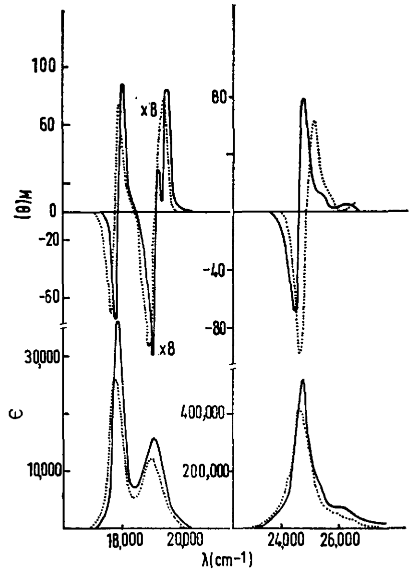

FIGURE 8 M.c.d. and absorption spectra of Cu(OEP) in polymethylmethacrylate. Dotted curves, room temperature; full curves *ca.* 8 K. $[\theta]_M$ and $\varepsilon$ are defined as in Figure 3

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[7] R. J. P. Williams, *Chem. Rev.*, 1956, **56**, 299.

[8] M. Zerner, H. Kobayashi, and M. Gouterman, *Theor. Chim. Acta*, 1966, **6**, 363.

and conjugative effect, the former arising from a change in potential at the nitrogen atoms due to different metals in the centre. Corwin[9] has related these shifts to the stability of the porphyrin. These aspects are discussed in greater detail in the references given. Cu(OEP) and Zn(OEP) have very similar $A/D$ values for both the $Q_0$ and the $B$ bands. The values for $Q_1$ however vary very widely from those of $Q_0$ and from each other. One possible explanation for this is that the excited state distorts strongly in the region of higher vibrational quanta. Alternatively, and more likely, it is due to the presence of vibronic $A$ terms of opposite sign which cancel the $Q_1$ m.c.d. partially and reduce $A/D$. This can be partly seen in the Zn(OEP) low-temperature spectrum. One point on the nature and extent of metal interaction which is appropriate here is that one might expect the ratio of intensities $Q_0/Q_1$ to reflect the extent of the interaction of the metal with the $\pi$ electrons of the ring. If the transition occurs with very little disturbance of the nuclear $\sigma$ framework then the 0–0 line will be much the strongest and the 0–1, 0–2 vibrations will only be excited when the excited potential-energy surface is somewhat distorted compared to the ground state. The $Q$ band is particularly sensitive to this and to other distortions since this band is invariably split by reduced symmetry inside the central region whereas the $B$ band shows very little splitting and usually we see only the 0–0 line.

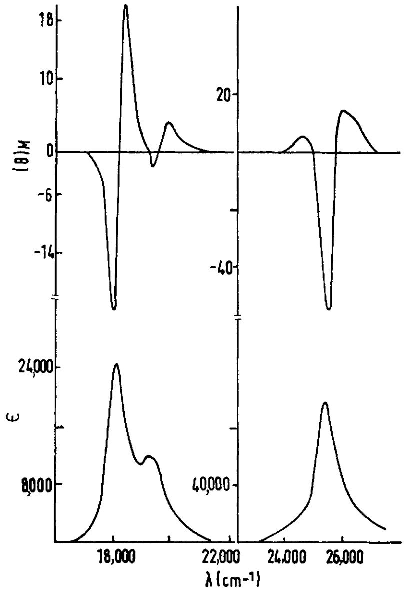

FIGURE 9 M.c.d. and absorption spectra of Co(OEP) in dichloromethane at room temperature. $[\theta]_M$ and ε are defined as in Figure 3

The change in m.c.d. between paramagnetic and diamagnetic metal is clearly seen to be fairly small, and this is surprising in a physical technique which is strongly dependent on ground- and excited-state magnetic moments. It is generally found at low temperatures that the ground state contribution is very large in paramagnetic species. That this does not dominate in the m.c.d. of Cu(OEP) at *ca.* 6 K is confirmation of the findings of Ake and Gouterman[10] that the wave functions of the metal are only very weakly coupled to those of the $\pi$-electron system. Coupling does exist, however, since the luminescence spectra are very sensitive to the nature of the metal and in the case of $Cu^{II}$ porphyrins, provide forbidden tripdoublet and quartet states from which emission takes place[10-12] indicating some degree of overlap between metal and porphyrin $\pi$-vibronic states. Our spectra of Cu(OEP) at room and low temperature show no evidence of transitions to the quartet or tripdoublet states. From the luminescence spectra the extinction coefficient for the tripdoublet is estimated to be *ca.* 70 l $mol^{-1}$ $cm^{-1}$ and we might expect to see this in m.c.d. since the technique is known to be particularly sensitive to certain spin-forbidden transitions. That we do not, suggests that it is a fairly broad line since the Faraday parameters are inversely proportional to the line width.

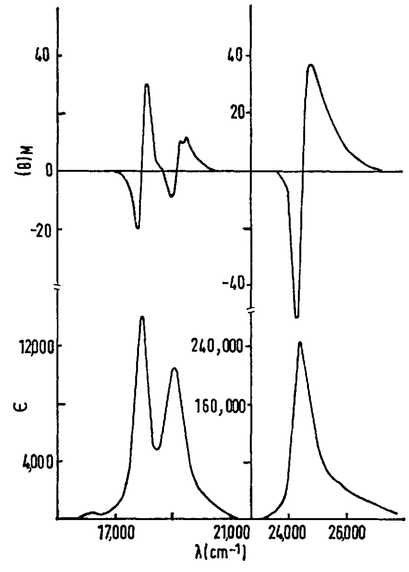

FIGURE 10 M.c.d. and absorption spectra of Ag(OEP) in dichloromethane at room temperature. $[\theta]_M$ and ε are defined as in Figure 3

In Cu(OEP) at low temperature a new feature develops in the region of the $Q_1$ band which has the appearance of a negative $A$ term superimposed on the predominantly positive $Q_1$ band. This is very likely an additional vibronic state, being a fundamental in a degenerate vibration of *ca.* 1300 $cm^{-1}$ in energy. An alternative explanation is that this is another electronic transition though none are predicted to lie in this region and the

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[9] D. G. Whitten, E. W. Baker, and A. K. Corwin, *J. Org. Chem.*, 1968, **28**, 2363.

[10] R. L. Ake, Ph.D. Thesis, Harvard University, 1968.

[11] R. L. Ake and M. Gouterman, *Theor. Chim. Acta*, 1969, **15**, 20.

[12] B. E. Smith and M. Gouterman, *Chem. Phys. Letters*, 1968, **2**, 517.

vibrational interpretation seems more likely. One feature of the Cu(OEP) spectrum is the extreme narrowness of the Soret band which is only some 600 cm$^{-1}$ broad compared to nearly 1000 cm$^{-1}$ in Zn(OEP). This also should give some measure of the extent to which the metal ' disturbs ' the $\pi$ system and it is interesting to note that the ratio of $Q_0/Q_1$ is somewhat greater in Cu(OEP) than in Zn(OEP), again some reflection of the mixing of $\sigma$ and $\pi$ orbitals by the metal.

The m.c.d. and absorption spectra of Zn(OEP) at low temperature show much more vibrational structure than Cu(OEP). As well as the familiar $Q_0$, $Q_1$ bands we see a negative $A$ term at 18,350 and a positive one at 19,150 cm$^{-1}$. The separations of these from $Q_0$ are 700 and 1400 cm$^{-1}$ respectively and it seems likely that these are the fundamental and first overtone in a normal mode which produces a degenerate vibronic state of opposite-sign m.c.d. for the 0–1 transition. The 0–2 transition then has the same sign as the origin.

The spectra of the free base at low temperature show an immense amount of vibrational structure. The complexity of the vibrational problem and the presence of over 30 normal modes [13] makes any analysis of these spectra very difficult. We can make one or two general statements however. The absorption spectrum shows a similar amount of structure to that published by Rimington *et al.*[13] which is of porphin in ethanol at $-180$ °C. We do not, however, detect any splitting of the $B$ band as did Rimington *et al.* and the m.c.d. shows an $A$-type term indicating that any splitting of the degeneracy is smaller than the band width.

The m.c.d. in this region is unusual and clearly suggests the presence of two or more transitions under the band in the spectrum of the free base. In fact it has the appearance of the superposition of two broad $A$ terms of opposite sign. The positive $A$ term clearly is analogous to that predicted and found in the metalloporphyrins and still retains its $A$ character despite the lower symmetry since the splitting is fairly small. The negative $A$ term is more difficult to account for. One possibility is that it is a vibronic component. The alternative is that it is a third electronic state lying underneath the $B$ band. Gouterman [14] has made identifications of the $N$ and $L$ bands which arise mainly from the transitions, $b_{2u} \longrightarrow e_g$ $a_{2u} \longrightarrow e_g$ respectively. These assignments are made mainly on the basis of agreement of position relative to the $B$ band with the MO calculations and may, therefore, have no basis in fact. It is possible that one of these transitions is responsible for the appearance of the opposite-signed m.c.d. in the free base and diacid spectra. This also occurs in the m.c.d. of Co(OEP) though now the new band is the lower in energy and also corresponds to the major part of the absorption peak. Presumably it is also present in the other metalloporphyrins but is masked by the strong $B$ band. Zn(OEP) shows a clearly defined positive $A$ term at 26,150 cm$^{-1}$ under the Soret band and this strongly suggests a vibrational overtone. The $Q$ bands show the familiar totally symmetric mode of *ca.* 13—1500 cm$^{-1}$ and we may pick out $Q_{x0}$, $Q_{x1}$ and $Q_{y0}$, $Q_{y1}$, quite easily from the room- or low-temperature absorption and m.c.d. spectra. On top of these seem to be several progressions in a low frequency (*ca.* 200 cm$^{-1}$) mode and it is clear that there are some degenerate vibronic states which, like the Soret band, are hardly split by the low-symmetry perturbation.

There is one interesting point which does not appear to have been discussed in previous work and yet is a particularly striking phenomenon. On passing from the metalloporphyrin to free base the degenerate $Q_{0,1}$ states are split by a low-symmetry perturbing potential $V_{D_{2h}}$ to the extent of *ca.* 2600 cm$^{-1}$, yet the Soret band is unsplit. It is, however, broadened and an upper limit on the separation of the $B_x$, $B_y$ components might be *ca.* 500 cm$^{-1}$. This is clearly a very specific perturbation and one might reasonably expect the theory to give some explanation for this. Before looking to the theories for a clue it is important to extract any symmetry information from the problem and we can do this in the following way.

The method used is analogous to that described by Griffith [15] in which we introduce the $D_{2h}$ perturbation by decomposing it into a sum of components of irreducible representations under $D_{4h}$. Since it belongs to the totally symmetric representation in $D_{2h}$ it can be written as a part transforming as $A_{1g}$ in $D_{4h}$ and another transforming as $B_{1g}$ in $D_{4h}$. This comes about because when the symmetry is lowered from $D_{4h}$ to $D_{2h}$, both $A_{1g}$ and $B_{1g}$ irreducible representations become $A_{1g}$ in the lower symmetry. The part transforming as $A_{1g}$ in $D_{4h}$ will not cause a splitting of levels but only an overall shift. That transforming as $B_{1g}$ will be responsible for breaking the degeneracy and we need only calculate the effect of a potential having this symmetry on the functions of the $D_{4h}$ porphyrin.

To do this we take the 50% C.I. functions of Gouterman redefined to conform to the Griffith operator convention of rotation of functions rather than coordinates.

$$\begin{aligned}
B_x &= 1/\sqrt{2}[a_{1u}e_x + a_{2u}e_y] \\
B_y &= 1/\sqrt{2}[a_{1u}e_y - a_{2u}e_x] \\
Q_x &= 1/\sqrt{2}[a_{1u}e_x - a_{2u}e_y] \\
Q_y &= 1/\sqrt{2}[a_{1u}e_y + a_{2u}e_x]
\end{aligned}$$

where $a_{1u}e_x$ represents the configuration $|a_{2u}{}^2a_{1u}{}^1\ e_{gx}{}^1\rangle$ for example.

The potential $V_{B_{1g}}$ causes a splitting of the doubly degenerate $e_g$ orbitals into the $x$ and $y$ components which can be written as

$$\begin{aligned}
\langle e_x|V_{B_{1g}}|e_x\rangle &= -1/\sqrt{2}\langle e||V_{B_1}||e\rangle \\
\langle e_y|V_{B_{1g}}|e_y\rangle &= +1/\sqrt{2}\langle e||V_{B_1}||e\rangle
\end{aligned}$$

using Table D 3·2 ref. 15.

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[13] C. Rimington, O. S. Kennard, and S. F. Mason, *Spectrochim. Acta*, 1968, **12**, 65.

[14] C. Weiss, K. Kobayashi, and M. Gouterman, *J. Mol. Spectroscopy*, 1965, **16**, 415.

[15] J. S. Griffith, ' The Irreducible Tensor Method for Molecular Symmetry Groups,' Prentice-Hall, New Jersey, 1962.

If we call the splitting due to the reduced symmetry $\mu$ then

$$\mu = 2/\sqrt{2}\langle e\|V_{B_1}\|e\rangle$$

$$i.e.\quad \langle e\|V_{B_1}\|e\rangle = \mu/\sqrt{2}$$

We can now use the two-electron formulae given by Griffith to evaluate matrix elements of the perturbing potential for the two excited configurations $|a_{1u}{}^1e_g{}^1\rangle$ and $|a_{2u}{}^1e_g{}^1\rangle$ and the $B$ and $Q$ states are simply linear combinations of these two configurations.

We can show that

$$\begin{aligned}\langle e_g{}^1a_{1u}{}^1\,{}^1E_u{}^{(2)}\|V_{B_1}\|e_g{}^1a_{1u}{}^1\,{}^1E_u{}^{(2)}\rangle &= 2\left[\langle e_g\|V_{B_1}\|e_g\rangle\, \mathrm{W}\begin{pmatrix}A_1EE\\ B_1EE\end{pmatrix}\right]\\ &= \langle e_g\|V_{B_1}\|e_g\rangle\end{aligned}$$

Hence
$$\langle {}^1E_{ux}{}^{(2)}|V_{B_1}|{}^1E_{ux}{}^{(2)}\rangle = -\,\mu/2$$
$$\langle {}^1E_{uy}{}^{(2)}|V_{B_1}|{}^1E_{uy}{}^{(2)}\rangle = +\mu/2$$

Similarly for $|a_{2u}{}^1e_g{}^1\rangle$, ${}^1E_u{}^{(1)}$

$$\langle {}^1E_{ux}{}^{(1)}|V_{B_1}|{}^1E_{ux}{}^{(1)}\rangle = \mu/2$$
$$\langle {}^1E_{uy}{}^{(1)}|V_{B_1}|{}^1E_{uy}{}^{(1)}\rangle = -\mu/2$$

*i.e.* the simple configuration states are split by equal amounts and in opposite directions by the low-symmetry perturbation.

If we take the C.I. states defined earlier and calculate the splittings we find

$$\langle B_x|V_{B1}|B_x\rangle = 1/\sqrt{2}(-\mu/2 + \mu/2)$$
$$\langle B_y|V_{B1}|B_y\rangle = 1/\sqrt{2}(+\mu/2 - \mu/2)$$

*i.e.* no splitting

$$\langle Q_x|V_{B1}|Q_x\rangle = 1/\sqrt{2}(-\mu/2 - \mu/2) = -\mu/\sqrt{2}$$
$$\langle Q_y|V_{B1}|Q_y\rangle = 1/\sqrt{2}(+\mu/2 + \mu/2) = +\mu/\sqrt{2}$$

*i.e.* a splitting of $\sqrt{2}\mu$, with $Q_x$ lower in energy than $Q_y$.

Thus the symmetry of the potential and the molecule suggests that for the simple configuration states that the splitting of $Q$ and $B$ bands should be equal in magnitude (though differing probably in their reduced matrix elements). However, if we take the mixed configurations as our new states we predict that the Soret band shall be unsplit and the visible band will split by $\sqrt{2}\mu$ as observed experimentally with $Q_x$ lower than $Q_y$ in agreement with m.c.d. and polarisation data.[16]

This procedure can also be used to predict the splitting in the $C_{2v}$ symmetry of the monoacid. Here we can show that the perturbing potential is again of $B_1$ symmetry and it results in a splitting of $\sqrt{2}\mu$ for the $Q$ bands (where $\mu$ in this case will have different magnitude to the $D_{2h}$ example) and zero for the $B$ band. Again the sign of the splitting will be such to place $Q_x$ lowest in energy.

One final useful feature is the linewidth of the $Q$ lines in the low-temperature free base spectrum. The theory of electronic band widths in polyatomic molecules is sufficiently developed that we are able to extract important information from their study.[17] Thus, with some approximations we may write the half width as [17–19]

$$\Delta E_{\frac{1}{2}} = E_v{}^2(n)\, F_n\rho(i)$$

where $E_v(n)$ is the vibronic coupling energy for the normal mode $n$ which mixes electronic eigenfunctions (this has a roughly constant magnitude of $10^3$—$10^4$ cm$^{-1}$ per Å nuclear displacement), $F_n$ is the Franck–Condon overlap factor representing the overlapping of vibrational eigenfunctions, and may vary very widely,[19,20] and $\rho(i)$ is the density of vibronic states (the so-called ' sea of states ') in the region of the electronic transition we are considering. These may arise from high vibronic levels of a lower electronic state or from the ground state or may be vibronic states of the host lattice. Thus if an allowed vibronic transition is overlapped by a dense background of states from a lower lying transition the line will be narrow for a low density and broad for a high density of states assuming that the other factors remain constant. (Note also that if the background of vibronic states stems from another excited state then we can make the generalisation that, if this other state is of different type to the first, $F_n$ may be large and the band broad. If they are of similar type, $F_n$ will be small and the band narrow). We can deduce that an electronic absorption band which becomes broader as we pass through the higher energies is suggestive of an underlying weak transition of different orbital type,[17] a $\pi$–$\pi$ perturbed by an $n \longrightarrow \pi$ for example or a linear state perturbed by a bent one. This is seen to be the case in the free base $Q$ bands where the $Q_{x1}$ line is considerably broader than $Q_{x0}$ and this may be due to an underlying $n \longrightarrow \pi^*$ transition. This theory predicts the second electronic state to be broader than the first which is the case in our spectrum.

Rates of internal conversion between excited states are obtainable from the band widths using the uncertainty relationship $\Delta E_{\frac{1}{2}}\,\Delta t = \hbar$. In using this we must subtract from the experimental line width, contributions from inhomogeneous broadening. The greatest of these would be the presence of multiple (and possibly distorted) sites in the polymer medium and widths of 10—100 cm$^{-1}$ are expected from this source. Lattice vibrations also contribute, though not to the extent of the multiple-site effect. If we take the upper limit of 100 cm$^{-1}$ this gives us a lifetime for the $Q_x$ state of *ca.* $10^{-13}$ s and a conversion rate of *ca.* $10^{-14}$ s for the $Q_y$ state.

## CONCLUSIONS

As a result of this study we can say that the simple theoretical picture accounts well for the gross features

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[16] B. G. Anex and R. S. Umans, *J. Amer. Chem. Soc.*, 1964, **86**, 5026.

[17] See for example R. M. Hochstrasser, *Accounts Chem. Res.*, 1968, **1**, 266.

[18] C. A. Coulson and K. Zalewski, *Proc. Roy. Soc.*, 1962, *A*, **268**, 437.

[19] M. Bixon and J. Jortner, *J. Chem. Phys.*, 1968, **48**, 715.

[20] J. P. Byrne, E. F. McCoy, and I. G. Ross, *Austral. J. Chem.*, 1962, **15**, 591.

of the absorption and m.c.d. spectra and that the metal orbitals do not interact strongly with those of the optical $\pi$ system in the metalloporphyrins we have examined. From the low-temperature spectrum of free base, OEP, we obtain evidence of an underlying forbidden band which may be an $n \longrightarrow \pi^*$ transition but we find no support at all for Corwin's suggestion that the four main visible bands are due to $n \longrightarrow \pi^*$ transitions. We have shown some theoretical justification for the fact that the visible band splitting on going from $D_{4h}$ to $D_{2h}$ is at least a factor of five as large as that of the Soret band. Finally, we find from the low-temperature spectra that the second band in the visible region $Q_1$, $Q_{x1}$, or $Q_{y1}$ invariably contains a number of superimposed vibronic states. This accounts for the mixed polarisation found in the polarised spectra by Anex and Umans.[16]

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