

Magnetic Circular Dichroism Studies. Part XXVI.¹ Magnetic Circular Dichroism Spectra of Porphyrin Dianions

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The m.c.d. spectra of alkyl-substituted porphyrin dianions show a positive A term for the Q_{0-0} band and unresolved A -terms in the Q_{0-1} band. A major difference with respect to the corresponding dications is the lower intensity of a negative A term for one vibronic component of the Q_{0-1} band in the dianions. Magnetic moments of 2.3—3.1 Bohr magnetons were obtained by curve fitting for the Q_{0-0} band. Moment analysis for the entire Q band gave smaller values of 0.6—1.5 Bohr magnetons. This discrepancy is interpreted to be a consequence of the weakly allowed character of the transition. The corresponding porphyrin dications were found to have smaller magnetic moments. Identification of the Q_{0-0} band in the m.c.d. spectrum of porphyrin dianion is difficult, because of its low intensity.

MAGNETIC circular dichroism (m.c.d.) has been of considerable value in gaining a better understanding of the electronic structure of porphyrins [skeletal structure (I)]

¹ Part XXV, P. M. Dolinger, M. Kielczewski, J. R. Trudell, G. Barth, R. E. Linder, E. Bunnenberg, and C. Djerassi, *Proc. Nat. Acad. Sci. U.S.A.*, in the press.

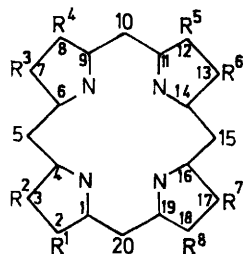
² W. T. Simpson, *J. Chem. Phys.*, 1949, **17**, 1218.

since the molecular parameters obtained can be directly compared with the results from theoretical calculations. All porphyrins which have D_{4h} symmetry (*e.g.*, metallo-complexes, dications, and dianions) are predicted²⁻⁴ to

³ H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, 1950, **18**, 1174.

⁴ M. Gouterman, *J. Mol. Spectroscopy*, 1961, **6**, 138.

be doubly degenerate in the first two excited states and as a consequence transitions to these states should exhibit A terms in the m.c.d. spectrum. This has been confirmed for a large number of metal chelates^{5,6} and dications⁷ all of which show positive A terms for the



(I)

a; octaethylporphyrin, $R^1-R^8 = \text{Et}$; b; deuteroporphyrin IX dimethyl ester, $R^2 = R^3 = R^5 = R^7 = \text{Me}$, $R^1 = R^8 = (\text{CH}_2)_2\text{CO}_2\text{Me}$, $R^4 = R^6 = \text{H}$. c; protoporphyrin IX dimethyl ester, $R^2 = R^3 = R^5 = R^7 = \text{Me}$, $R^1 = R^8 = (\text{CH}_2)_2\text{CO}_2\text{Me}$, $R^4 = R^6 = \text{CH}_2 = \text{CH}$

lowest excited state ($A_{1g} \rightarrow E_u^1$ or Q band) and the next higher excited state ($A_{1g} \rightarrow E_u^2$ or S band). Quantitative evaluation of the spectral data yielded excited state magnetic moments^{5,8} that were in surprisingly good agreement with those predicted from the simple free-electron model of Simpson.² Even better correspondence was achieved when more detailed M.O. calculations were made.⁹

We report here for the first time † m.c.d. spectra of porphyrin dianions and compare the experimental values of their magnetic moments with those obtained for the corresponding dications, whose spectra were reported previously.⁷

EXPERIMENTAL

M.c.d. measurements were carried out with a JASCO UV/ORD-5 spectropolarimeter modified to allow c.d. measurements and equipped with a superconducting magnet built by Lockheed Palo Alto Research Laboratories (model OSCM 103).¹⁰ The magnetic field strength was 49.5 kG. $[0]_M$ Values are given in degree $\text{cm}^2 \text{dmol}^{-1} \text{G}^{-1}$. The solvent system used for preparing the dianions from the neutral porphyrins was a mixture of dimethyl sulphoxide-toluene-water (8 : 1 : 1 v/v) whose sodium hydroxide concentration was 0.02N. No attempt was made to exclude oxygen from the solutions. Porphyrin concentrations were approximately $2-4 \times 10^{-5} \text{M}$. The porphyrin dianion solutions were found to be unstable and in particular to be extremely sensitive to light. Handling of the solutions was therefore carried out in the dark and spectra were taken within 1 h.

* In a previous publication⁷ we labelled a normal A term as negative, in agreement with the convention of McHugh *et al.*⁹ In this and subsequent publications we will conform to the convention of Stephens *et al.*^{8,11} and will call an A term positive when the value of A is positive, and *vice versa*.

† In a recent publication H. Rein, K. Ruckpaul, and W. Haberditzel (*Chem. Phys. Letters*, 1973, **20**, 71) have reported m.o.r.d. spectra of porphyrins in alkaline media. We attribute their failure to observe A terms for the Q_{0-0} band to sample decomposition prior to measurement (see Experimental section).

⁵ E. A. Dratz, Ph.D. Thesis, University of California, Berkeley, 1966.

⁶ R. Gale, A. J. McCaffery, and M. D. Rowe, *J.C.S. Dalton*, 1972, 596.

Scanning of the spectral region 350–450 nm caused extensive decomposition of the sample with the result that the m.c.d. spectra of the dianions in the Soret region could not be obtained. Scanning in the visible region had no effect on the sample. The dication spectra were obtained in benzene solution containing trifluoroacetic acid (0.1N).⁷ The porphyrins used in this study were all of chromatographic purity and were obtained from the following sources: octaethylporphyrin, Professor H. H. Inhoffen; deuteroporphyrin IX dimethyl ester, Pfaltz and Bauer; protoporphyrin IX dimethyl ester, Mann Research Laboratories; porphin, Professor M. Gouterman. Dimethyl sulphoxide (Spectrograde) was obtained from Matheson, Coleman and Bell and toluene (reagent grade) from B and A.

The spectra were converted into digital form using a Calma model 302 graphical digitizer (resolution ± 0.01 in). The digitized data were then transferred to the IBM 360/50 digital computer at the Stanford University Medical School Computer Facility, normalized by standard equations and plotted on a Calcomp plotter. Spectral bands were fitted with the 'variable wing model' described in detail in ref. 7. Because of the better separation between the Q_{0-0} band and the Q_{0-1} band in the m.c.d. spectrum as compared to the absorption spectrum, the m.c.d. A term was fitted first, letting the wing parameter (a), half bandwidth, amplitude, and centre frequency vary freely. Subsequently, the absorption band was fitted using the same wing parameter. The values of this parameter were in the range 0.6–0.7, indicating that the experimental band shapes are neither Gaussian ($a = 0$) nor Lorentzian ($a = 1$). The zeroth and first moments of the absorption and m.c.d. spectra were calculated according to the procedure outlined by Stephens *et al.*¹¹

RESULTS AND DISCUSSION

Porphyrins can be considered to be very weak acids which in the presence of a strong base will form dianions by proton abstraction. Their absorption spectra¹²⁻¹⁴ are very similar to those of the dications, showing a weak Q_{0-0} band, a more intense Q_{0-1} band, and a strong Soret band. The m.c.d. and absorption spectra of octaethylporphyrin dianion are shown in Figure 1. A strong positive A term is associated with the Q_{0-0} absorption band at $17,000 \text{ cm}^{-1}$. The m.c.d. of this transition is termed⁹ 'normal' and may be considered to be characteristic of a porphyrin with D_{4h} symmetry. Although the vibronic components of this band overlap, with the result that only a broad band (at $18,200 \text{ cm}^{-1}$) is observed in the absorption spectrum, a complicated pattern of bands is found in the m.c.d. spectrum that is quite different in appearance from the corresponding

⁷ G. Barth, R. E. Linder, E. Bunnenberg, and C. Djerassi, *Ann. New York Acad. Sci.*, 1973, **206**, 223.

⁸ P. J. Stephens, W. Suëtaka, and P. N. Schatz, *J. Chem. Phys.*, 1966, **44**, 4592.

⁹ A. J. McHugh, M. Gouterman, and C. Weiss, *Theor. Chim. Acta*, 1972, **24**, 346.

¹⁰ S. R. Hawkins and J. H. Harshman, *Rev. Sci. Instruments*, 1967, **38**, 50.

¹¹ P. J. Stephens, R. L. Mowery, and P. N. Schatz, *J. Chem. Phys.*, 1971, **55**, 224.

¹² G. D. Dorrough, J. R. Miller, and F. M. Huennekens, *J. Amer. Chem. Soc.*, 1951, **73**, 4315.

¹³ T. I. Strelkova and G. P. Gurinovich, *Biofizika*, 1968, **13**, 1164.

¹⁴ J. A. Clarke, P. J. Dawson, R. Grigg, and C. H. Rochester, *J.C.S. Perkin II*, 1973, 414.

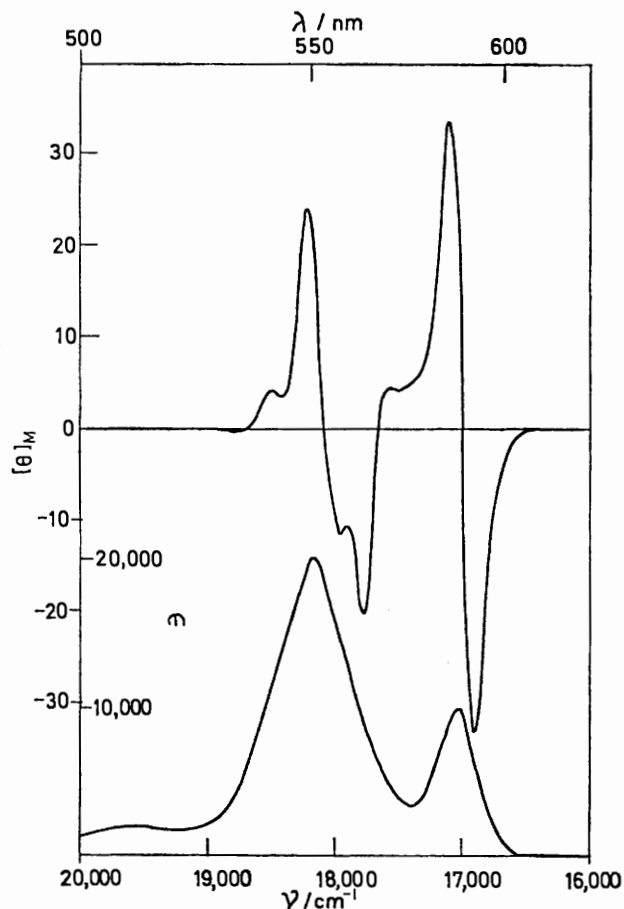


FIGURE 1 M.c.d. (upper curve) and absorption (bottom curve) spectra of octaethylporphyrin dianion

dication spectrum (see Figure 1 of ref. 7). In particular, the quite intense negative A term, separated by 622 cm^{-1} from the Q_{0-0} band in the dication is of much lower intensity in the dianion spectrum (at $\nu_{0-0} + 660\text{ cm}^{-1}$). Strong positive A terms at *ca.* 1100 cm^{-1} above the Q_{0-0} band are present in the spectra of both ionic species.

influence of the magnetic field (rigid shift model¹¹) the magnetic moment can be calculated from $\mu_{0-0} = 2A/D$ (Bohr magnetons) where A , the m.c.d. A value, and D , the dipole strength, can be obtained by standard curve fitting procedures from the spectral data.^{5,8} The results for three different porphyrins are given in the Table. Octaethylporphyrin the most symmetric molecule among our examples, shows the highest value of $\mu_{0-0} = 3.1$ Bohr magnetons. Lower values were observed for deuteroporphyrin IX dimethyl ester dianion ($\mu_{0-0} = 2.3$) and protoporphyrin IX dimethyl ester dianion ($\mu_{0-0} = 2.4$). The m.c.d. spectrum of the latter compound is characterized by a lack of fine structure within the vibronic region caused by band broadening. Indeed, only a single positive A term at $17,750\text{ cm}^{-1}$ is observed. These values of the dianions are therefore lower than the moments obtained for metalloporphyrins, which range from 4 to 7 Bohr magnetons depending on the central metal.⁵

The magnetic moments of the dications (Table) were found to be consistently smaller by 20–30% compared with the corresponding dianions. This difference is even more pronounced if one compares the magnetic moments for the entire Q band. An extreme example is porphin where μ is four times higher for the dianion than for the dication. An explanation for this difference without detailed M.O. calculations can only be speculative. It is, however, interesting that calculations made by Sundbom,¹⁵ assuming both ionic species to be planar, indicate that the density distribution of the π electrons may be quite different in the two cases. The dications were calculated to have a considerably higher π electron density at the nitrogen atoms. This contraction of the π electron cloud could reduce the angular momentum and account for the lower magnetic moment of the dications. Unfortunately, moments were not calculated against which to check this suggestion. A similar argument was made by Dratz⁵ to explain the dependency of the magnetic moment on the metal.

Molecular parameters

Compound		D	D_{0-0}	A^*	A_{0-0}	μ	μ_{0-0}	Γ m.c.d./u.v.	ν_{0-0}
Octaethylporphyrin	Dianion	11.6	2.4	6.8	3.8	1.2	3.1	260/360	17,005
	Dication	10.5	2.0	3.4	2.3	0.65	2.3	265/370	16,905
Deuteroporphyrin IX dimethyl ester	Dianion	10.7	1.6	3.6	1.8	0.67	2.3	260/410	17,040
	Dication	9.5	1.6	1.7	1.2	0.36	1.5	255/400	16,970
Protoporphyrin IX dimethylester	Dianion	12.0	3.8	9.0	4.5	1.5	2.4	410/570	16,675
	Dication	10.3	2.2	2.5	2.3	0.49	2.1	360/535	16,680
Porphin	Dianion	8.4		4.1		0.98			
	Dication	8.8		1.0		0.23			

D = Dipole strength in (Debye)²; A = m.c.d. A value in Bohr magneton (Debye)²; μ = magnetic moment in Bohr magneton; Γ = half bandwidth in cm^{-1} ; ν_{0-0} = centre frequency of m.c.d. A term in cm^{-1} . The subscript 0-0 refers to the Q_{0-0} band otherwise the value is for the total Q band.

* In Table 1 of ref. 7, the sign of the A values for the dications has been given incorrectly.

Since a similar m.c.d. band pattern, differing only with respect to the resolution and magnitude of the components, was observed for deuteroporphyrin dianion, these features seem to be characteristic for alkyl-substituted porphyrin dianions.

Assuming that the bands are rigidly shifted under the

In any event, the observation of positive A terms and magnetic moments comparable with those of metalloporphyrins indicates that the symmetry of the absorbing species must closely resemble the D_{4h} point group. Since absorption intensity variations of the Q band with the

¹⁵ M. Sundbom, *Acta Chem. Scand.*, 1968, **22**, 1317.

particular alkali metal¹² indicate an association between dianion and metal, our data support the suggestion made by Strelkova and Gurinovich¹³ that alkali-metals are bound by Coulomb interaction in such a way that they are located along the four-fold symmetry axis thus preserving the D_{4h} symmetry of the molecule.

An alternative method for spectral analysis and computation of magnetic moments was recently introduced by Stephens *et al.*,¹¹ which has the advantage that it is not dependent on a particular band shape and therefore especially useful in those cases where the vibronic components of an electronic band are unresolved from its 0-0 band. For a totally allowed transition both methods will give identical results,¹¹ but will differ to the extent that this condition is not fulfilled. As can be seen from the Table, the magnetic moments for the Q band obtained by moment analysis are considerably smaller than those obtained for the Q_{0-0} band by the fitting procedure discussed earlier. This result is also obvious from a qualitative comparison of the Q_{0-0} and Q_{0-1} band intensities. Whereas the Q_{0-0} band is of lower intensity than the Q_{0-1} band in the absorption spectrum (Figure 1), the reverse is true for the intensity distribution in the m.c.d. spectrum. We interpret this result as being a direct consequence of the partially forbidden character of this transition which gains intensity by vibronic borrowing from the allowed E_u^2 state (Soret band). Perrin *et al.*¹⁶ have predicted that this mechanism will lead to sign inversion of the A terms for some vibronic components, with respect to the sign of the Q_{0-0} band. The unresolved vibronic components with oppositely signed A terms would then tend to cancel each other and thus result in an overall reduction of m.c.d. intensity. Negative A terms, although clearly observable in the dication spectra, are much weaker in the dianion spectra. The higher $\mu_{0-0} : \mu$ ratio for the dications seems to reflect this difference. Nevertheless, in the dianions, the magnetic moment of the Q_{0-0} band is still larger than the moment for the whole Q band by a factor of 2-3. The question of whether this is due to the presence of further unresolved negative A terms or to the generally lower $A : D$ ratio of the vibronic bands cannot be answered from the poorly resolved spectra of the dianions.

The spectra (Figure 2) of porphin dianion require special comment since their interpretation is complicated by the difficulty of locating the very weak Q_{0-0} band. A similar situation was observed in the porphin dication spectra where it could be demonstrated⁷ by low temperature measurements that some of the long wavelength bands are hot bands. In the m.c.d. spectrum of porphin dianion (Figure 2), an A term of apparently negative sign at 17,100 cm^{-1} appears to correspond to the Q_{0-0} band which is seen as a broad shoulder at 17,000 cm^{-1} in the absorption spectrum. This assignment, however, would be very difficult to accept, both on theoretical grounds⁹ and from the experimental fact that the A terms of the Q_{0-0} band of all D_{4h} porphyrins thus far investigated are positive. It must also be remembered that, for weak transitions, B term contributions⁵ cannot be neglected

since their intensities decrease only with the square root of D whereas the A term intensity is directly proportional to the dipole strength. This, together with the possible presence of hot bands, can result in m.c.d. band patterns which preclude the immediate recognition of an A term. The vibronic part of the spectrum is dominated by a positive A term at 18,170 cm^{-1} .

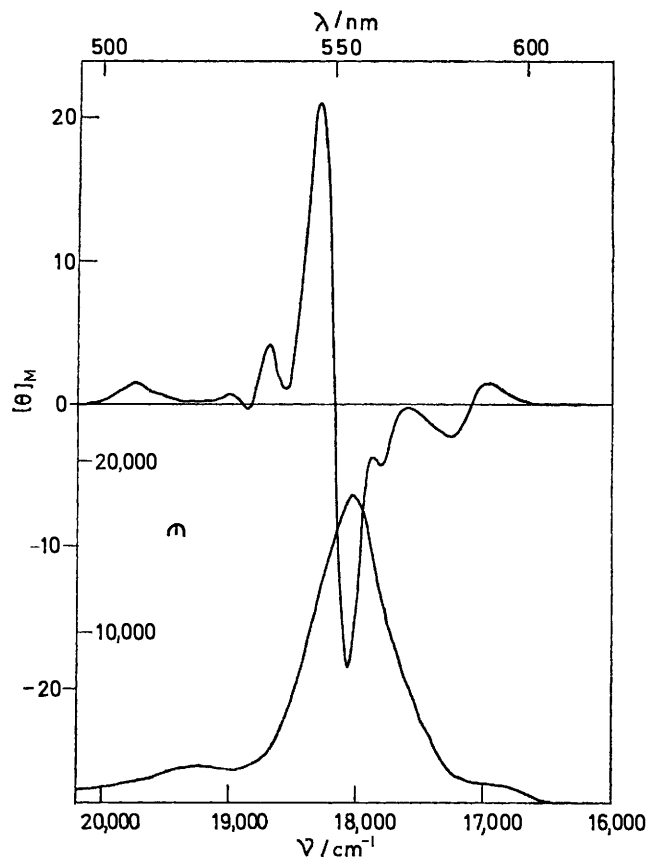


FIGURE 2 M.c.d. (upper curve) and absorption (bottom curve) spectra of porphin dianion

Finally, we comment on the observation that the half-bandwidth of the Q_{0-0} band was consistently found to be 20-30% lower in the m.c.d. spectrum than in the absorption spectrum (Table). This can be rationalized if one assumed that solvent-solute interactions lead to a zero field splittings of the excited state and that those species that have a large splitting contribute proportionally less to the total m.c.d. than to the absorption band as compared to the unperturbed molecules. Similar results were observed for metalloporphyrins and will be discussed in more detail in a subsequent publication.

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¹⁶ M. H. Perrin, M. Gouterman, and C. L. Perrin, *J. Chem. Phys.*, 1969, **50**, 4137.