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NOVEL MAGNETIC CIRCULAR DICHROISM SPECTRA OF MONOACETYL PORPHYRINS. STRUCTURE IMPLICATIONS.[1†]

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Summary: The unexpected observation of a pair of oppositely signed MCD bands within the Q_0^x transition of monoacetyl porphyrins is related to the existence of equilibria between N-H proton tautomers and/or conformational populations of the acetyl substituent.

Substituent-induced sign variation is a pervasive phenomenon in the MCD spectra of organic molecules. For porphyrin derivatives, it is particularly well documented for reduced porphyrins[2] and for metalloporphyrins having electron withdrawing substituents such as heme a.[3] For free-base porphyrins, sign variation has been reported only for protopheophytin a[4] where the effect of the vinyl and carbonyl substituents on opposing rings gives rise to sign inversion of the Q_0^x, Q_0^y, and Soret MCD bands as compared to those of octaethylporphyrin.[5]

As part of a general program of study, we have examined the MCD spectra of porphyrins having a single electron withdrawing pyrrole ring substituent and have found that the monoacetyl porphyrin 1[6] quite unexpectedly exhibits (Fig. 1) a pair of oppositely signed MCD bands for the Q_0^x transition, a weak positive band for the Q_0^y transition, and the normal uninverted sign pattern for the Soret (B) MCD band system. In order to confirm this finding, 2-acetyldeuteroporphyrin IX dimethyl ester (2) was synthesized.[7] Its absorption and MCD spectra are virtually coincident with that of 1 (Fig. 1).

We believe that the most direct interpretation of these results is that MCD may provide direct optical access to two important structural events for porphyrins—the existence of N-H proton tautomer and/or substituent group conformational equilibria. The basis for this contention, illustrated in Fig. 2, stems from Michl's perimeter model for the MCD of cyclic π-electron systems[8] and from our elaboration of it for substituted porphyrins.[2] In its simplest form the model predicts that when the relative magnitudes of the differences in energies of the four frontier molecular orbitals are such that ΔHOMO > ΔLUMO, then the sign pattern of the MCD bands of the four-orbital purely electronic transitions should be -+-+, with increasing energy; whereas, if ΔHOMO < ΔLUMO, then the sign pattern should be the inverted one, +-+-.

The relative magnitudes of the orbital energy differences previously adduced[2] for octaalkyl porphyrins is ΔHOMO > ΔLUMO and for them the normal, -+-+, sign pattern is consistently ob-

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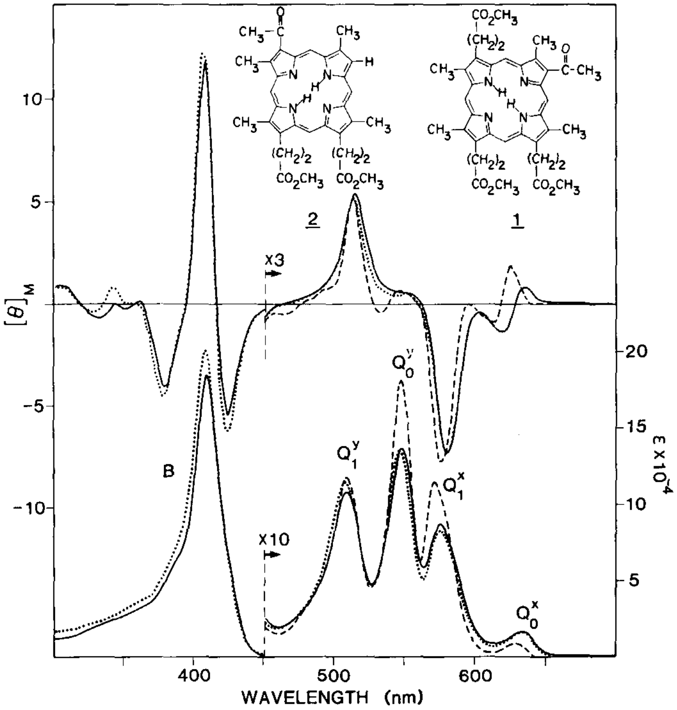
[†] Dedicated to Robert Maxwell, founder and publisher of Pergamon Press, on the occasion of his sixtieth birthday.



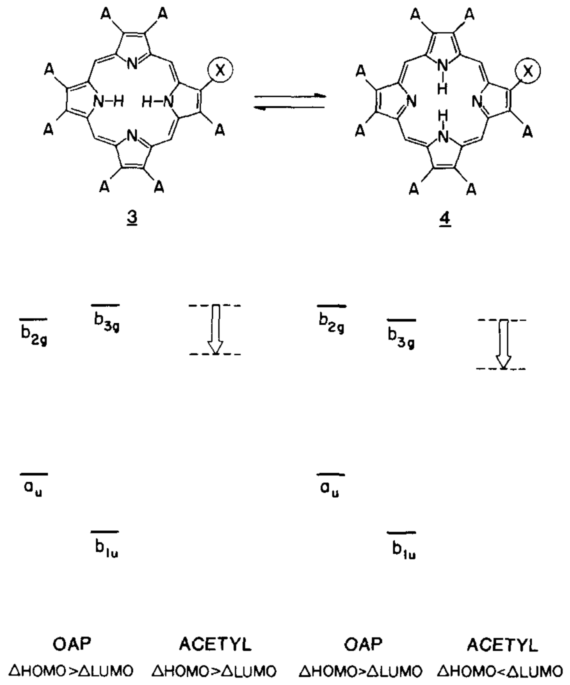


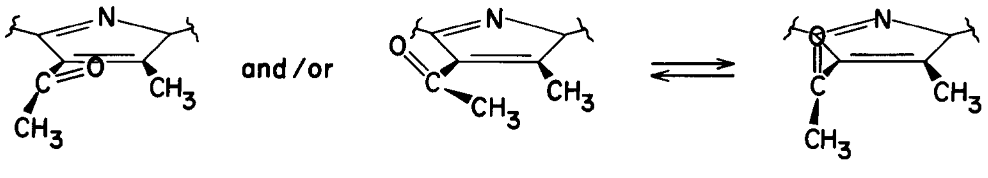
Figure 1 (Left). The MCD and absorption spectra of 1 (——) and 2 (···) in $CHCl_3$ at 23° are almost coincident. MCD and absorption spectra of 1 (---) in CH_2Cl_2 at -74° are shown *only for the visible region.*

Figure 2 (Right). HOMO and LUMO energy level diagrams for the "horizontal" (3) and the "vertical" (4) tautomers of an octaalkyl porphyrin (X = A) are shown as solid lines. The principal orbital energy level shifts (compare the electron density maps *in Fig. 2 of ref. 2) due to the acetyl substituent for each tautomer* are indicated by the arrows and the dashed lines.

served.[2,5] The ordering of the LUMO orbitals (b_{2g} and b_{3g}, Fig. 2) depends on whether the trans N-H protons are along the horizontal (3) or vertical (4) axes, but ΔLUMO is the same for both tautomers. However, when an electron withdrawing group replaces one alkyl group, its dominant effect is to lower the energy of one of the LUMO orbitals (here, b_{3g}) and the magnitude of ΔLUMO now depends critically on the positions of the protons in the two tautomers. We suggest that ΔHOMO > ΔLUMO for the "horizontal" acetyl porphyrin tautomer (3) but that ΔHOMO < ΔLUMO for the "vertical" tautomer (4). In the MCD spectrum (Fig. 1), the "horizontal" tautomer should then give rise to the negative part of the Q_0^x MCD, the positive Q_0^y MCD, and the normal sign pattern of the Soret MCD band system. On the other hand, the "vertical" tautomer would then be responsible for the positive lobe of the Q_0^x MCD and the expected negative MCD band for its Q_0^y transition would act to diminish the positive contribution to this transition from the "horizontal" tautomer. Since $|\Delta\text{HOMO} - \Delta\text{LUMO}|$ is presumed to be small for the "vertical" tautomer, sign inversion in the Soret would not necessarily be expected for it.[2,8]

As a test of this tautomer hypothesis, the MCD of 1 in CH_2Cl_2 was measured at -74° (Fig. 1). The positive lobe of the Q_0^x MCD increases and a negative contribution to the Q_0^y MCD becomes evident. This is the result expected for an increase in the population of the energetically preferred "vertical" tautomer (4 in Fig. 2) at the lower temperature. We also find that the N-H resonances of 1 are split in the ^{1}H NMR spectrum at about -74°. While this result could be a consequence of self aggregation,[9] we find that the MCD spectrum of 1 at 23° remains invariant over a hundred-fold concentration range. Thus, aggregation can be excluded as a cause of the double banded MCD spectrum.

An alternative explanation, and one that will need to be considered conjunctively with the tautomer hypothesis, is that, because of the delicate balance proposed for the relative splitting of the HOMO's and LUMO's of 1 and 2, MCD effectively "sees" two populations of conformers of the acetyl group, 5 and 6. In one (5), optimum (but not maximum, because of steric interactions) overlap of the acetyl and porphyrin orbitals obtains; whereas, in the other (6), overlap is minimal. The first population should exhibit inverted MCD; the MCD of the second should show the normal band sign pattern. This conformational equilibrium should also be temperature dependent and biased in the direction of the more coplanar conformers (5) at lower temperatures. This explanation is thus also consistent with experiment (Fig. 1).



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We anticipate that our preliminary MCD findings will ultimately lead to new perspectives and information about the structures of substituted porphyrins. Since very little is known about the tautomeric equilibria of substituted porphyrins[10] or about the solution conformations of chromophoric substituents,[11] we are presently attempting to resolve these questions through the synthesis of appropriate sterically hindered and unhindered acetyl (and other) porphyrins, through continuing ^{1}H and ^{15}N NMR studies of selectively labeled analogs of 1, and through all valence electron MO calculations.

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