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Substituent-Induced Sign Variation in the Magnetic Circular Dichroism of Free-Base Porphyrins with a Single Electron-Withdrawing Substituent. The Question of N–H Proton Equilibrium[1]

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Abstract: Absorption and magnetic circular dichroism (MCD) spectra are reported for a series of monosubstituted free-base alkylporphyrins possessing vinyl, oxime, cyano, ethoxycarbonyl, acetyl, and formyl substituents. The porphyrins are alkylated at all peripheral pyrrole positions except that adjacent to the π-substituent. This pattern of alkylation allows for the first time a direct comparison between the MCD of substituted benzenes and free-base porphyrins. Comparison with substituted benzenes, and with the homologous β-methylporphyrin series, permits the coupled effects of central-proton tautomerism and substituent conformation on MCD to be disentangled and their separate contributions estimated. Independent and confirming measurements of the trans tautomer equilibrium and its influence on MCD are obtained from temperature studies. The occurrence of sign inversion is found to be sensitive to small shifts in tautomer equilibrium, as well as to changes in π-substituent conformation. The interpretation of substituent and central-proton effects on MCD in the context of Michl's perimeter model is supplemented by explicit INDO–CI calculations of B terms.

Sign inversion in the magnetic circular dichroism (MCD) spectra of porphyrin derivatives is most commonly observed in porphyrins with an electron-withdrawing substituent at a peripheral position,[4-10] although it can also occur in reduced porphyrins,[11] some D_{4h} porphyrins,[4,12-15] and in a few symmetrically substituted porphyrins of lower symmetry.[16] While the occurrence of substituent-induced sign variation is well-established for specific cases, until recently there has been no experimental or theoretical study of the MCD and absorption spectra of a series of porphyrins with peripheral substituents presenting a systematic variation of electron-donating or -accepting demand upon the porphyrin ring.

In a previous paper[17] the MCD and absorption spectra of the free-base series **1b,c,e,f,g**, with vinyl, cyano, ethoxycarbonyl, acetyl, and formyl substituents, respectively, were examined for the effects of central proton tautomerism and substituent conformation. This series presented a range of substituent perturbation strengths and observed MCD behavior. Vinyl porphyrin **1b**, with the weakest substituent perturbation, exhibited normal MCD;[18] while in formyl porphyrin **1g**, at the other end of the range of substituent perturbations, the MCD bands of the visible electronic transitions, Q_0^x and Q_0^y, were completely inverted. The temperature dependence of the long-wavelength MCD implied that N–H proton

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(18) The sign pattern of $[\phi]_M$ observed for the purely electronic bands of octaethylporphyrin: $-+-+$ with increasing energy.

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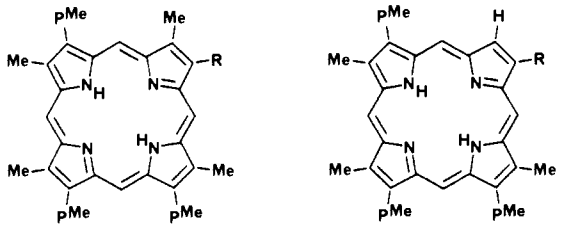

1 2

1a, **2a**	R =	H
1b, **2b**	R =	$CH{=}CH_2$
1c, **2c**	R =	CN
1d, **2d**	R =	CH=NOH
1e, **2e**	R =	$CO_2C_2H_5$
1f, **2f**	R =	$COCH_3$
1g, **2g**	R =	CHO

Figure 1. Structures of the metal-free monosubstituted porphyrins investigated. Central protons are depicted in the "vertical" orientation. Me = methyl, p = propionate.

tautomerism modulated the observed MCD of the porphyrin free bases with strong electron-withdrawing groups, but there was also evidence in the MCD of carbonyl porphyrins to indicate that this influence was entangled with the conjunctive effects of substituent conformation. Out-of-plane conformers were expected to be most dominant for the bulkiest carbonyl substituent. The observation of monosignate, uninverted MCD in (ethoxycarbonyl)porphyrin **1e**, as opposed to the bisignate MCD of the acetylporphyrin **1f**, indicated that the steric bulk of the carbonyl substituent could indeed by a significant factor associated with sign variation—presumably by determining the homogeneity or heterogeneity of conformer populations, and thus influencing the relative contribution by each conformer of its characteristic MCD signature to the observed MCD. The π-acceptor strengths of the acetyl, ethoxycarbonyl, and cyano moieties were such as to bring the porphyrins **1c**, **1e**, and **1f** near the condition of a soft chromophore, in Michl's terminology[19] (vide infra), where the purely electronic MCD tends to vanish. The possible importance of vibronic contributions[20] in this region further complicated the analysis for structural effects. A detailed consideration of the MCD and absorption spectra band shapes indicated the presence of vibronic effects in the long-wavelength MCD of the cyanoporphyrin **1c**, the chromophore with the weakest visible band MCD in the series.

Removal of the appropriate alkyl group from the periphery of the porphyrins in series **1** is expected, for reasons explained below, to alter the pattern of long-wavelength MCD magnitude and sign toward a pattern more characteristic of a negative-hard chromophore and away from the ambiguities of the soft chromophore case. Significantly, such a structural modification can also perturb both the steric constraints on substituent conformation and the relative stability of N-H proton tautomers, thereby providing a probe of these equilibria and their interrelationship. A systematic study of the tautomer-conformer interrelationship with ^1H and ^{15}N NMR is difficult due to synthetic effort and cost; consequently, we turn to examination of the evidence presented by the MCD spectra of homologous porphyrins, guided by both theoretical models and explicit calculations, as the most appropriate means of obtaining a general understanding of the several effects that are operative.

In the present work, we present a study of the MCD of the monosubstituted porphyrin free-base series, **2a–g**, which is formally obtained from the porphyrin series **1a–g** by removal of the methyl adjacent to the π-acceptor substituent. The synthesis of the demethyl porphyrin (DMP) series provides a basis for more direct comparison of substituent effects in substituted benzenes and porphyrins than is possible in the **1** series. Comparisons of the MCD of the demethylporphyrins with the corresponding substituted benzenes and with the methyl porphyrins (P), **1**, will be used, along with temperature studies of MCD, to assess the importance of conformational and tautomeric effects in the monosubstituted free-base porphyrins. Theoretical analysis of sign inversion from the viewpoint of the four-orbital model[17] is extended in the present work by direct calculation of B terms from INDO-CI wave functions.

We find that the subtle change in structure presented by demethylation has a large effect on the MCD associated with the long-wavelength visible bands, an effect which permits the extensive elicitation of structural information about these monosubstituted porphyrins. The work presented here is also essential to studies of porphyrins which contain multiple π-substituents, a class than contains many naturally occurring porphyrins. Furtheremore, it may also be pertinent to understanding the biological function of metalloporphyrins, e.g., heme a, as protein prosthetic groups, since variations in substituent nature and stereochemistry can be expected to play a role in modulating such interactions.

Methods

Absorption and MCD spectra were obtained and analyzed for band positions and integrated intensities as described earlier.[17]

Michl's perimeter model[19] was used to gain a qualitative understanding of the effect of structural perturbations upon MCD. The important conclusion of this algebraic model of MCD in perturbed $(4N + 2)$-electron annulenes is the pivotal importance of the sign of the quantity ΔHOMO–ΔLUMO in determining the sign of the MCD associated with the lower energy electronic transitions. The applicability of the perimeter model to molecules that can, at least formally, be regarded as perturbed $(4N + 2)$-electron n-annulenes has been reviewed by Michl.[21] Because the LUMO's of D_{4h} porphine dianion are degenerate by symmetry, while the HOMO's are nearly degenerate, porphine dianion serves as the reference for a four-orbital model[22] or porphyrins that is closely analogous to the perimeter model of annulenes. This model has been extensively applied to explain the occurrence of sign inversion in the MCD of reduced and substituted porphyrins.[15-17,19a,b,23]

The perturbation theory expression employed to calculate the B terms is

$$B(a\rightarrow j) = \mathrm{Im}\{\sum_{k\neq a} \langle k|\mu|a\rangle\cdot\langle a|\mathbf{m}|j\rangle \times \langle j|\mathbf{m}|k\rangle/(E_k - E_a) + \sum_{k\neq j} \langle j|\mu|k\rangle\cdot\langle a|\mathbf{m}|j\rangle \times \langle k|\mathbf{m}|a\rangle/(E_k - E_j)\} \quad (1)$$

where μ and $\mathbf{m}$ denote the magnetic and electric moment operators, respectively, and E_a, E_j, and E_k are the energies of states a, j, and k, respectively.[24] The application of semiempirical methods to the calculation of B terms from eq 1 has been investigated by Warnick and Michl.[25] They concluded from their MCD calculations for nonalternant hydrocarbons that the variations of calculated B values that resulted from reasonable variations in the choice of coordinate origin, and from variation of the extent of CI employed, were sufficiently small that meaningful results could be obtained from such calculations. Varying the coordinate origin as much as 1 Å about the center of the porphyrin macrocycle had a negligible effect on calculated B values in the present study.

State wave functions were obtained from an Intermediate Neglect of Differential Overlap/Configuration Interaction (INDO/CI) method.[26]

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(20) See ref 17 for discussion of vibronic interactions in MCD and absorption spectra of cyanoporphyrin.

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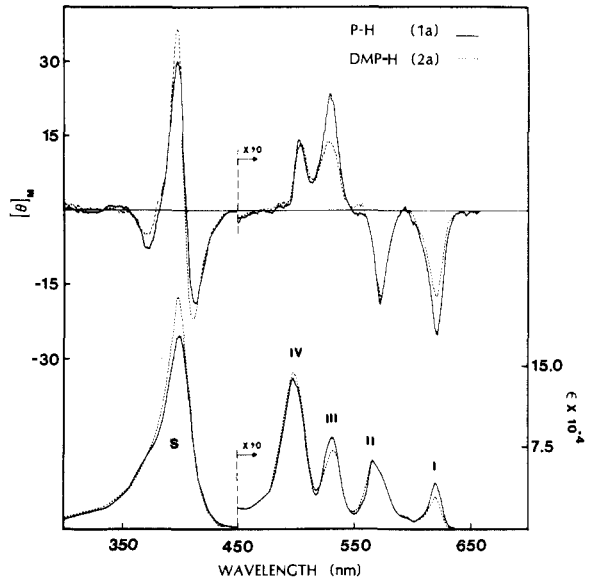

Figure 2. Absorption and magnetic circular dichroism spectra of unsubstituted methylporphyrin (**1a**) (—) and demethylporphyrin (**2a**) (···) in chloroform.

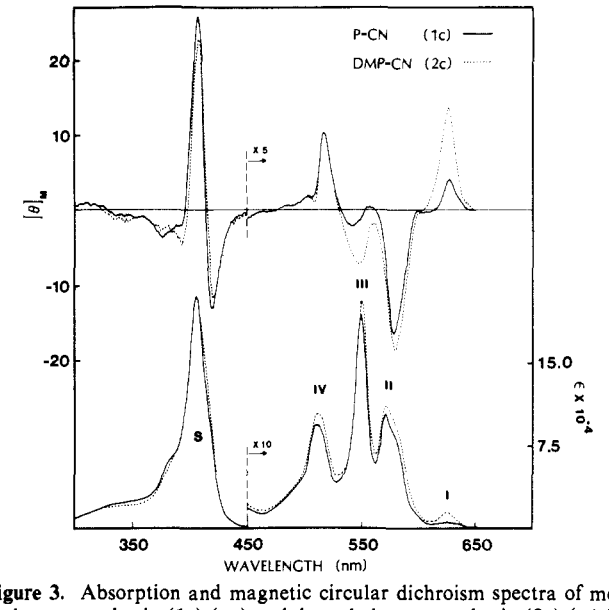

Figure 3. Absorption and magnetic circular dichroism spectra of methylcyanoporphyrin (**1c**) (—) and demethylcyanoporphyrin (**2c**) (···) in chloroform.

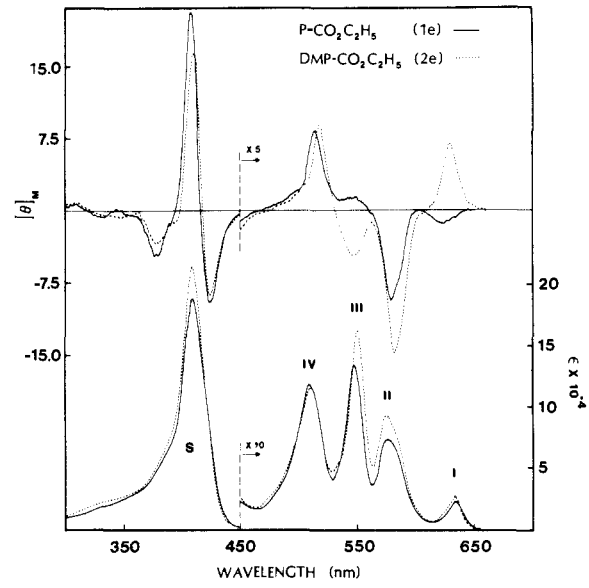

Figure 4. Absorption and magnetic circular dichroism spectra of methyl(ethoxycarbonyl)porphyrin (**1e**) (—) and demethyl(ethoxycarbonyl)-porphyrin (**2e**) (···) in chloroform.

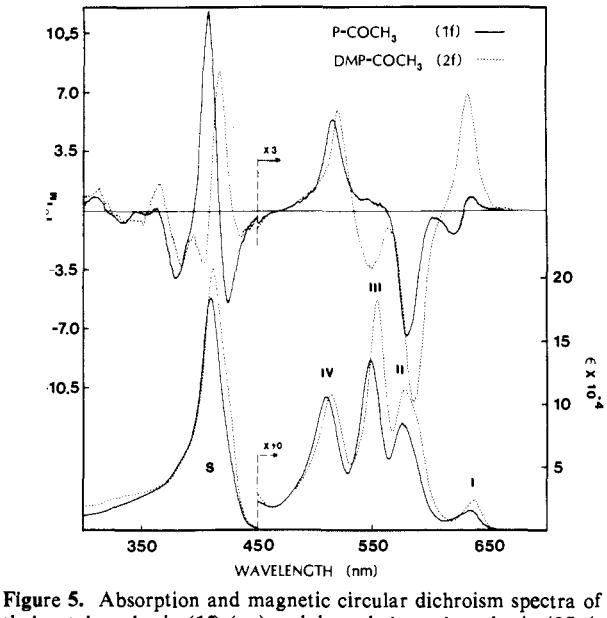

Figure 5. Absorption and magnetic circular dichroism spectra of methylacetylporphyrin (**1f**) (—) and demethylacetylporphyrin (**2f**) (···) in chloroform.

The INDO/S parameterization, in particular, has been successfully used to calculate *B* terms for a series of small heterocycles.[27] However, a previous study[17] of the MCD of a series of monosubstituted porphyrins found that this parametrization of INDO gave frontier orbital energy differences that did not correlate, in the context of the Michl model,[19] with the MCD sign inversion observed in some of these substituted porphyrin macrocycles.

We employed a second parametrization of the INDO method in order to evaluate its suitability in calculating the MCD of free-base porphyrins. INDO/S′ differed from INDO/S principally in the choice of resonance integral parameters for carbon and nitrogen. The values originally adopted by Pople[28] for CNDO and INDO (−21.0 and −25.0 eV for β_C^0 and β_N^0, respectively) were employed in INDO/S′, which resulted in average π resonance integrals of −2.99 and −2.74 eV, respectively, for C–C and C–N neighbors—increases of 24 and 7% over the INDO/S values. A second small difference was that the empirical Mataga–Nishimoto form for the electron repulsion integrals[26e] was retained from INDO/S without the factor due to Weiss.[29] In all other aspects of INDO/S′ prescription was the same as that of INDO/S.

Peripheral alkyl groups were not explicitly included in the calculations presented here. The electronic influence of the peripheral alkyl groups is only implicitly included, in the parametrization, and the applicability of the INDO/S′ parametrization to porphyrins presenting a pattern of alkylation greatly different from those in the present study is uncertain.

The configuration interaction included the 196 lowest energy singly excited configurations, a configuration set that extended well above 60 000 cm^{-1} in energy. Double excitations were not included since they make little direct contribution to the MCD associated with transitions arising out of the ground state.[30] The sum over states in eq 1 was truncated at 100 CI states, a cutoff that was well above those intermediate states that were found to make substantial contributions to the

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(29) The f_γ factor added in ref 26a to the Mataga-Nishimoto formula has been set to unity in INDO/S′ in order to reduce overestimation of the Q–B band splitting.

(30) Inclusion of double excitations could indirectly affect the MCD of ground-state transitions through the energy denonimator in eq 1. However, preliminary calculations showed that inclusions of doubly excited configurations had little effect on the Q^x–Q^y state splitting; therefore, visible band MCD would be little changed.

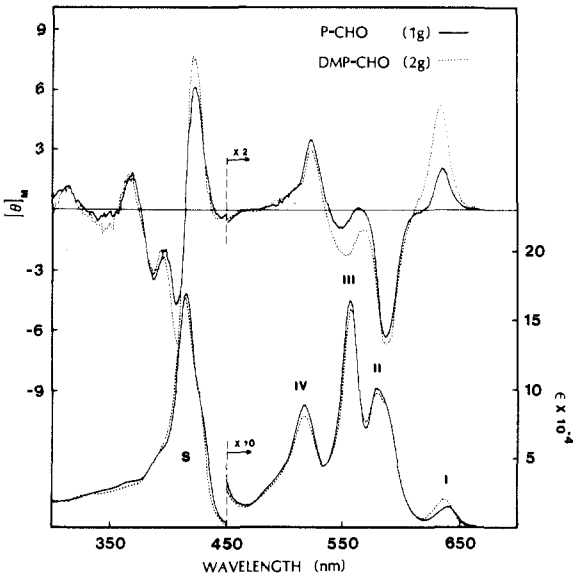

Figure 6. Absorption and magnetic circular dichroism spectra of methylformylporphyrin (**1g**) (—) and demethylformylporphyirn (**2g**) (···) in chloroform.

MCD associated with visible and near-UV transitions. Matrix elements of the magnetic moment operator, μ, over the AO basis were obtained with the Linderberg relation.[31] The dipole length form was used to calculate absorption intensities. Löwdin deorthogonalization[32] was not applied in the calculation of the AO matrix elements due to computational constraints imposed by the large sizes of the molecules studied. The effect of neglecting Löwdin deorthogonalization in the calculation of the B terms of the Q_0^x and Q_0^y transitions is expected to be small (vide infra). Porphyrin and substituent geometries were the same as employed earlier,[17] with substituents in a planar orientation with respect to the ring.

Results and Discussion

The absorption and MCD spectra of selected demethyl porphyrin (DMP series) free bases are presented in Figures 2–6, with the spectra of the corresponding P series compound (methyl group adjacent to π substituent) overlayed for comparison. Spectral data for the DMP series are summarized in Table I. The labeling of spectral bands, sign conventions for $[\theta]_M$ and B values, and the choice of coordinate axes and symmetry labels are identical with those employed previously.[17]

The MCD associated with the electronic bands of lowest energy is generally most sensitive to substituent effects,[17] and it is there that the important spectral differences arise between the demethyl- and methylporphyrin series; both the UV-vis absorption spectra and the MCD associated with the Soret bands of the DMP series (**2**) are little changed from the P series (**1**) spectra, as would be expected for such closely similar sets of compounds. For a discussion of the absorption spectra and Soret band MCD of the vinyl-, cyano-, (ethoxycarbonyl)-, acetyl-, and formylporphyrins the reader is referred to our earlier contribution.[17]

The principal differences between the visible-band MCD spectra of the DMP and the P series of porphyrins are (1) the absence of bisignate MCD in the DMP series and (2) the broader incursion of sign inversion in the DMP series. The MCD of the Q_o^x transition is entirely monosignate throughout the DMP series, in contrast to the bisignate MCD observed for the Q_o^x transition in P–$COCH_3$ (Figure 5) and P–CN (Figure 3); similarly, the MCD of the Q_o^y transition is entirely monosignate throughout the DMP series, while the Q_o^y MCD of P–CN is bisignate. In addition, the B values associated with the Q_o^x band are shifted to more negative values throughout the DMP series: the porphyrins substituted with the four strongest electron-withdrawing groups—cyano, ethoxycarbonyl, acetyl, and formyl—all have inverted visible band MCD. Indeed, the (ethoxycarbonyl)porphyrin changes sign entirely between the two series (Figure 4): the Q_o^x MCD of **1e** is monosignate and negative (sign of $[\theta]_M$) and the corresponding band in **2e** is monosignate and positive.

In order to assess the contribution of structural effects—π-substituent conformation and tautomerism—to the divergence in visible-band MCD observed for the DMP and P series porphyrins we will use the MCD of the substituted benzenes as a reference. First, however, we must consider the direct electronic effect of the methyl group adjacent to the π-substituent.

Electronic Effect of Peripheral Alkyl Groups. All of the monosubstituted porphyrins examined in the present and previous[17] study are substituted with methyl or methylpropionate groups at all of the pyrrole sites remaining on the periphery, with the exception in the DMP series of the site adjacent to the π-substituent. Alkyl groups donate electron density to the porphin π-system[22] and can be classified as weak -E substituents.[33] While the electronic effect of an alkyl or quasi-alkyl group on the porphyrin π-system is small, such effects are clearly evident in the absorption and MCD spectra of octaethylporphyrins.

The electronic effect of peripheral alkyls is apparent in the much greater intensity of the long-wavelength absorption band of octaethylporphine dianion ($\epsilon_{max}(Q_0)/\epsilon_{max}(Q_1)$ ratio of 0.49) than is observed in porphine dianion (ϵ ratio of 0.06)[15a] and is also evident in the larger peak $[\theta]_M$ values seen in zinc octaethylporphine, as compared to zinc porphine.[34] This effect has an explanation in terms of perturbed orbital energies: while symmetric peripheral substitution of alkyl groups has no net effect on the LUMO splitting of a D_{4h} porphyrin, it does exert a significant influence on ΔHOMO. Electron donation from alkyl groups to the porphin π-system destabilizes the b_2 (a_{1u}) HOMO relative to the b_1 (a_{2u}) HOMO (Figure 7 in ref 17), which has negligible density at the peripheral pyrrole-ring carbons. In this way alkylation increases the size of ΔHOMO, which in the four-orbital model[22] is connected to the long-wavelength absorption intensity of D_{4h} porphyrins.

The electronic effect of alkylation is also evident in the MCD spectra of free-base porphine and octaethylporphyrin. The central protons split the LUMO's in energy and stabilize the b_1 orbital relative to the b_2. The effect on relative HOMO energies is larger, since the AO coefficient for nitrogen is larger in the b_1 orbital than it is in the LUMO's (Figure 7 in ref 17). The result in porphine free base is that ΔHOMO is slightly larger than ΔLUMO; hence, the visible band MCD is weak but normal.[35] The additional destabilizing effect of the alkyl groups on the b_2 orbital gives octaethylporphine free base a still larger value of ΔHOMO, which results in a peak $[\theta]_M$ value for the Q_0^x band that is nearly an order of magnitude larger than that for porphine free base.[17]

Replacement of a peripheral alkyl group with various π-acceptor substituents, as in the free-base P series, gives additional stabilization of the lower energy LUMO while now stabilizing the b_2 relative to the b_1 MO. If the π-acceptor is of sufficient strength, this leads to the condition ΔHOMO < ΔLUMO and inverted visible-band MCD is observed, e.g., P–CHO (Figure 6). Removal of a second alkyl group on the π-substituted pyrrole ring, as in the DMP series, or from the oppositely situated pyrrole, lowers electron density in the c_1 and b_2 orbitals and moves the orbital energy differences toward the condition of ΔHOMO < ΔLUMO. This is seen most clearly by comparing the visible band MCD of **1a** and **2a** in Figure 2, porphyrins for which the effects of substituent conformation and tautomerism on MCD are absent or negligible: the demethylporphyrin has a markedly reduced intensity of MCD in the electronic bands (shift to less positive band I B values).

It is natural to also consider briefly the direct and indirect contributions of alkylation to spectral shifts. Although the shifts

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Table I. MCD and Absorption Spectral Data of Monosubstituted Demethyl Free-Base Porphyrins[a]

compd[b]	spectrum	MCD:[c,d] $\lambda_{max}/[\theta]_M/10^4B$ ABSN:[e,f] $\lambda_{max}/10^{-3}\epsilon/D$ Soret and near-UV region							Q_1^y IV[d,f]	Q_0^y III	Q_1^x II	Q_0^x I
OEP	MCD	332	347	375	399	413			504	531	572	620
		−0.9	1.3	−10.6	28.2	−16.0			1.4	2.8	−1.8	−3.1
									−11.05	−26.27	11.0	22.02
	ABSN	330 (s)	352 (s)	376 (s)	399				498	534	566	619
		18.1	34.5	87.0	171.3				13.8	10.5	6.2	4.9
				157					6.50	2.9	2.4	1.0
DMP-H (**2a**)	MCD			370	398	411			504	528	574	622
				−5.0	36.2	−21.3			1.3	1.3	−1.6	−1.6
									−10.96	−15.80	11.19	11.95
	ABSN	323 (s)	346 (s)	371 (s)	399				497	533	566	620
		15.4	28.8	65.9	211.1				14.4	7.2	6.4	2.9
				127					7.13	2.86	2.38	0.64
DMP—CH=CH_2 (**2b**)	MCD	331	353	379	405	424			510	532	579	626
		−0.4	1.2	−7.1	20.2	−12.5			1.4	1.7	−1.8	−1.9
									−11.29	−21.73	14.0	17.2
	ABSN	330 (s)	360 (s)	373 (s)	406				504	543	573	631
		16.7	39.9	62.6	174.9				13.6	11.9	7.1	4.3
				162					7.65	3.83	2.92	1.14
DMP-CN (**2c**)	MCD	335 (s)	346	375	394	409	422		517	547	579	625
		−1.0	−1.4	−2.4	−3.5	19.3	−9.7		2.0	−1.4	−3.6	2.7
									−13.49	14.37	36.01	−19.91
	ABSN	333 (s)	358 (s)	382 (s)		407	417 (s)		512	551	571	625
		21.2	23.6	58.2		212.8	117.7		10.4	20.6	11.1	1.5
				134					5.31	4.95	4.24	0.48
DMP-CH=NOH (*E*-**2d**)	MCD	335	350	383	411	424			517	548	580	626
		−1.3	0.5	−6.5	19.9	−9.8			1.5	0.4	−3.3	−0.5
									−20.50	−2.98	20.40	5.80
	ABSN	337 (s)	359 (s)	384 (s)	410				510	550	574	634
		22.3	34.2	73.6	175.5				9.9	13.8	8.4	2.0
				124					6.16	4.80	4.36	0.43
DMP—CH=NOH (*Z*-**2d**)	MCD	330	350	380	409	425			516	543	581	626
		−0.7	0.8	−6.3	19.9	−11.6			1.7	0.6	−2.4	−1.1
									−20.27	−8.95	22.22	7.68
	ABSN	332 (s)	357 (s)	386 (s)	409				508	549	574	634
		22.8	37.0	82.7	203.0				12.1	14.4	8.9	2.2
									7.34	5.67	4.58	0.50
DMP-$CO_2C_2H_5$ (**2e**)	MCD	330	350	378	394	409	424		517	547	582	629
		−0.5	−0.7	−3.4	−1.2	16.3	−8.7		1.8	−0.9	−2.9	1.4
									−15.84	10.51	28.77	−12.09
	ABSN	330 (s)	355 (s)	385 (s)		409	420 (s)		510	551	574	633
		23.1	28.9	66.3		214.8	116.8		11.6	16.2	9.2	2.7
				148					7.27	4.3	4.0	0.73
DMP-$COCH_3$ (**2f**)	MCD	333 (s)	348	365	385	404	418	437	521	550	586	633
		−0.3	−0.5	1.7	−3.2	−3.1	8.3	−1.5	2.0	−1.1	−3.7	2.3
									−17.95	13.16	39.86	−20.57
	ABSN	335 (s)		366 (s)	388 (s)		413	424 (s)	514	556	578	637
		27.3		35.5	63.1		208.6	117.5	10.7	18.2	11.1	2.3
					140				6.53	5.57	5.1	0.65
DMP-CHO (**2g**)	MCD	335 (s)	345	367	388	408	423	443	523	554	588	634
		−0.4	−0.9	1.5	−3.1	−6.5	7.7	−0.4	1.5	−1.1	−3.3	2.6
									−13.03	14.65	37.35	−23.98
	ABSN	340 (s)		366 (s)	392 (s)		414	427 (s)	516	557	579	638
		25.3		31.1	54.4		167.3	90.7	8.1	15.8	9.8	2.1
									5.68	4.66	4.43	0.66

[a] Principal spectral features evident in chloroform solutions. Essentially identical spectra were obtained in dichloromethane. [b] Structures are given in Figure 1. [c] Wavelength in nanometers; s = shoulder; molar magnetic ellipticity, $[\theta]_M$, in deg cm^2 dmol^{-1} G^{-1}; values of the *B*-term, *B*, are in $D^2 \cdot \beta_e/cm^{-1}$. [d] In the visible region, *B* values were extracted directly by a full band curve-fitting protocol, except for band I for which zeroth moment values are given. As in ref 17, vibronic intensity on the blue side of band IV was ignored. In the Soret region, the spectral analysis was guided by the deconvoluted absorption band positions. [e] Wavelength in nanometers; s = shoulder; molar extinction coefficient, ϵ, in 1000 cm^2 mol^{-1}; values for the dipole strength, *D*, are in D^2. [f] In the visible region values for the dipole strength were obtained by a direct full band curve-fitting protocol (see ref 17). Vibronic intensity on the blue side of band IV was ignored. In the Soret region spectral deconvolution was accomplished by simultaneous fitting of the absorption curve and its derivative.

Table II. Difference between Q_0^x Absorption Energies of P-X and DMP-X Porphyrins

substituent	$\bar{\nu}_{DMP} - \bar{\nu}_P$ (cm^{-1})[a]
H	0
$CH{=}CH_2$	-120
CN	200[b]
$CO_2C_2H_5$	0
$COCH_3$	-50
CHO	50

[a] Calculated from $\lambda_{DMP}(Q_0^x)$ values from Table I and $\lambda_P(Q_0^x)$ values from ref 17, Table I. [b] Taken from band Ia, long-wavelength shoulder of a vibronic band.

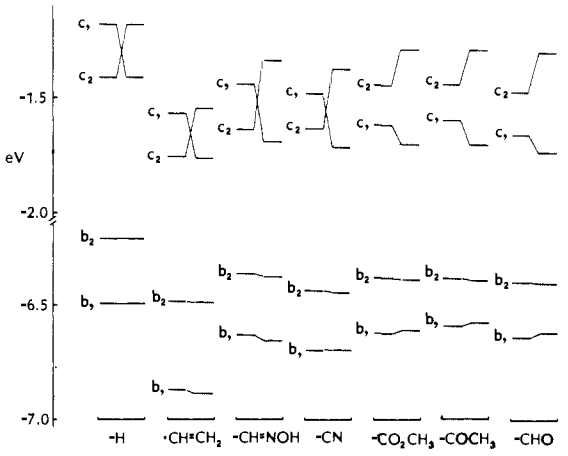

Figure 7. INDO/S', HOMO, and LUMO energies of free-base monosubstituted model porphyrins (DAP-X). Energy levels of horizontal tautomers are on the left.

in Q_0^x absorption band energies between the DMP-X and P-X porphyrins (Table II) are quite small, two conclusions can be drawn. First, the first entry in Table II indicates that the replacement of a peripheral methyl group with a hydrogen appears to have no direct effect on spectral energy, which is not surprising. Second, four of the five porphyrin–homologue pairs with π-substituents do show a shift, and the porphyrins with substituents that are expected to have the least steric interaction with the adjacent methyl show the most positive shifts. The explanation for this trend is not obvious but will become apparent after the explication below of structural effects in monosubstituted porphyrin free bases.

Comparison with MCD of Substituted Benzenes. The measured *B* values of the Q_0^x transition in the DMP series are plotted, in Figure 8, vs. the *B* values for the ^1L_b transition of the corresponding substituted benzenes. The *B* values of the Q_0^x transition in the P series are plotted for comparison. The occurrence of sign inversion in the demethylporphyrins is paralleled in each of the corresponding substituted benzenes, with the exception of vinylbenzene, where vibronic contributions are considered to be important.[36] This is not the case for the P series: **1e** (ethoxycarbonyl) and **1f** (acetyl) do not show the negative *B* value observed for the corresponding benzene derivative.

Much information about subtle details of structure is contained in a plot of MCD such as Figure 8, since the observed shifts in *B* values are much larger than the uncertainties in their measurement. Notice that the ordinate and abscissa are not scaled equally in Figure 8—the larger electronic transition moments and magnetic moments of the porphyrins contribute to the larger range of *B* values observed in the porphyrins. While the responses of the porphyrin and benzene π-systems to an electron-withdrawing substituent are not identical (here defined as giving the same incremental change in ΔHOMO–ΔLUMO), the reasonable correlation in Figure 8 to a linear relationship indicates that their responses are roughly proportional. The linear regression lines have positive intercept values because **1a** and **2a** are positive-hard

(36) Kaito, A.; Tajiri, A.; Hatano, M. *J. Am. Chem. Soc.* **1976**, *98*, 384.

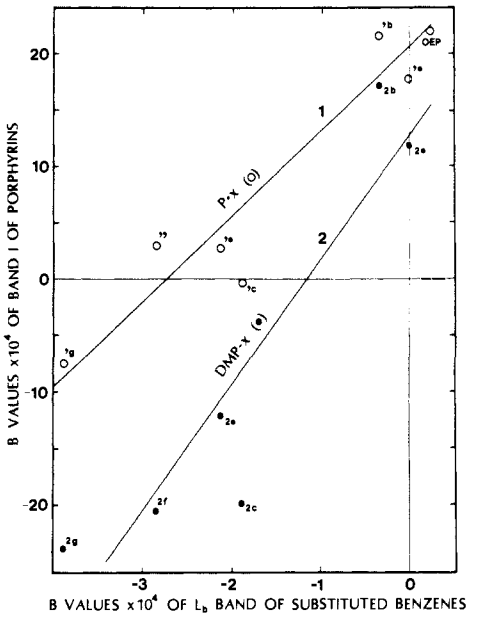

Figure 8. *B* values of band I of monosubstituted methylporphin free bases (series **1**) (ref 17) and demethylporphyrin free bases (series **2**) vs. *B* values of the ^1L_b band of corresponding monosubstituted benzenes (ref 17).

chromophores while benzene is double soft (ΔHOMO = ΔLUMO = 0). For this reason the occurrence of sign variation in the porphyrins requires a $+E$ substituent of appreciable strength, while even a weak π-acceptor can induce MCD sign inversion in the benzenes.

The linear regression lines for the two series are both shifted and skewed from one another. The shift can be attributed to the electronic effect of the methyl group (vide supra), which raises all of the band I *B* values of the P series by an additive constant value, approximately $10^{-3}\ \beta_e \cdot D^2/cm^{-1}$, over the DMP series values. The skew is attributed to the conjunctive effects of shifts in tautomer and, for the carbonyl substituents, conformer equilibria induced by the peripheral methyl group. Both effects will contribute to decreasing the slope of curve 1 (i.e., stabilizing the horizontal tautomers of compounds toward the left of Figure 8).

The tautomer distribution is connected to the substituent π-acceptor strength because it is electron withdrawal from pyrrole nitrogens to the π-substituent that is responsible for inequality of tautomer energies. The predominance of vertical tautomers (trans protons on non-π-substituted pyrrole-rings [see Figure 1]) is expected to increase with the π-acceptor strength of the substituent, with the caveat that rotation of substituent conformation may modulate the effective electron-withdrawing strength of the carbonyl substituents. The influence of a peripheral methyl group on the N-H proton equilibrium can then be seen to come about in two ways: (1) a direct effect, by stabilizing protonation of the nearby pyrrole nitrogen through electron donation, and (2) an indirect effect, steric interference with a carbonyl substituent. The presence of the methyl acts through both effects to stabilize the horizontal tautomers. A shift in tautomer or conformer equilibria induced by peripheral methylation would cause curves 1 and 2 to pivot about their *y*-intercepts, which remain approximately fixed. If the equilibria are identical in corresponding derivatives, then the two curves will be parallel. A stabilization of the horizontal tautomer will decrease the slope of the line. The contribution from the shift in tautomer equilibrium alone to the skew between curves 1 and 2 is best seen from the disproportionate distance between points for **1g** and **2g** when compared to the *y*-intercepts.

Changes in substituent conformation between the DMP and P series can be inferred from the distribution of points for the carbonyl-substituted porphyrins **1e,f,g** and **2e,f,g** in Figure 8. While the reasonably small scatter about the regression lines suggests that conformer effects for these substituents of varying steric bulk are not grossly disproportionate in either porphyrin

Table III. Comparison of Experimental and Calculated Spectral Parameters for Visible Bands of Vertical and Horizontal Tautomers

	experimental			INDO/S′			INDO/S		
	$B \times 10^{4}$ [a]	f [b]	kk	$B \times 10^{4}$	f	kk	$B \times 10^{4}$	f	kk
				(a) Vertical Tautomers					
				DMP-H (**2a**)					
Q_x	11.95	0.025	16.1	17.94	0.001	16.4	50.78	0.010	15.3
Q_y	−15.80	0.067	18.8	−6.85	0.097	19.4	−57.65	0.065	17.9
				DMP—CH=CH_2 (**2b**)					
Q_x				54.78	0.009	16.4	87.16	0.024	13.8
Q_y				−52.43	0.136	19.1	−102.38	0.088	16.4
				DMP—CH=NOH (**2d**)					
Q_x	5.80	0.039	15.8	2.89	0.001	16.3	52.05	0.006	13.9
Q_y	−2.98	0.098	18.2	15.89	0.181	19.0	−59.27	0.141	16.6
				DMP-CO_2R (**2e**)					
Q_x	−12.09	0.038	15.8	−33.97	0.002	16.2	32.40	0.002	13.8
Q_y	10.51	0.104	18.1	62.58	0.170	18.9	−33.36	0.111	16.2
				DMP-$COCH_3$ (**2f**)					
Q_x	−20.57	0.046	15.7	−37.68	0.002	16.2	29.62	0.002	13.8
Q_y	13.16	0.107	18.0	67.89	0.169	18.8	−30.01	0.113	16.1
				DMP-CN (**2c**)					
Q_x	−19.91	0.039	16.0	−9.34	0.001	16.3	40.32	0.004	15.3
Q_y	14.37	0.091	18.1	30.89	0.150	19.1	−42.89	0.100	17.7
				DMP-CHO (**2g**)					
Q_x	−23.98	0.041	15.7	−40.26	0.002	16.2	31.03	0.002	13.8
Q_y	14.65	0.091	18.0	70.81	0.181	18.8	−32.43	0.120	16.1
				(b) Horizontal Tautomers					
				DMP—CH=CH_2 (**2b**)					
Q_x	17.20	0.032	15.8	51.80	0.010	16.3			
Q_y	−21.73	0.104	18.4	−50.91	0.099	19.1			
				DMP—CH=NOH (**2d**)					
Q_x				31.52	0.009	16.1			
Q_y				−27.20	0.089	19.0			
				DMP-CO_2R (**2e**)					
Q_x				28.26	0.013	16.1			
Q_y				−24.46	0.053	19.1			
				DMP-$COCH_3$ (**2f**)					
Q_x				29.23	0.012	16.0			
Q_y				−26.32	0.050	19.1			
				DMP-CN (**2c**)					
Q_x				31.60	0.006	16.2			
Q_y				−26.82	0.067	19.2			
				DMP-CHO (**2g**)					
Q_x				28.12	0.015	16.0			
Q_y				−25.44	0.049	19.0			

[a] Units are $\beta_e \cdot D^2/cm^{-1}$. [b] Oscillator strength.

series from that encountered in the benzene series, there are, nevertheless, several indications of conformational change.

The first of these is the greater drop in B value for acetylporphyrin from the P series (**1f**) to the DMP series (**2f**) relative to formyl- and (ethoxycarbonyl)porphyrins. This suggests that loss of steric interference allows a more planar conformer to dominate in DMP-$COCH_3$, while the formyl is relatively unhindered in both porphyrin series and the greater steric bulk of the ethoxycarbonyl moiety minimizes any freedom of movement resulting from demethylation of **1e**. Second, a shift in tautomer equilibrium will accompany greater effective π-acceptor strength of the carbonyl substituents and augment the trend to negative B values in the DMP series. This augmented shift of the acetylporphyrin and, to a much lesser extent, of the (ethoxycarbonyl)porphyrin is seen in the shift of the regression line for the DMP series to fall significantly below the DMP-CHO data point, which does not benefit from an appreciable augmentation. Finally, modulation of π-substituent strength by conformation is seen even in the weakly perturbing vinyl substituent: the data point for **2b** is farther above its regression line than is the **1b** point.[37]

To summarize the discussion of Figure 8, three interrelated effects on MCD resulting from methylation have been discerned: (1) the direct electronic effect of replacing a single peripheral methyl group with a hydrogen, (2) an indirect effect through shifting of the tautomer equilibrium, and (3) an indirect effect through alteration of substituent conformation and the additional shift in tautomer equilibrium this causes. The influence on B values of each of these effects is of the same order of magnitude, $10^{-3}\ \beta_e \cdot D^2/cm^{-1}$. Additional evidence from temperature studies for the effect of tautomer equilibrium on MCD will be considered below.

Calculated B Values. The calculated B values for the vertical and horizontal tautomers of the dealkylporphyrin free-base (DAP-X) series are presented in Tables III, parts a and b, respectively. The DAP-X series is derived from the DMP-X series by replacing all of the peripheral alkyl and quasi-alkyl groups with hydrogens, and it serves as a computationally simpler model.

(37) The importance of vibronic contributions to L_b band MCD of styrene indicates that the electron-donor and -acceptor nature of the vinyl substituent nearly cancel in styrene.

Table IV. Contribution of Q_x,Q_y coupling to MCD of Q_x ($\beta_e \cdot D^2/cm^{-1}$)[a]

DAP-X[b]	$F^{Q_x}_{Q_xQ_y} \times 10^4$	$B \times 10^4$	$\mu_{Q_xQ_y}$ (β_e)
CH=CH_2	68.86	54.78	5.08
H	20.68	17.94	5.19
CH=NOH	3.02	2.89	5.04
CN	-10.70	-9.34	5.10
CO_2CH_3	-38.72	-33.72	5.01
$COCH_3$	-42.88	-37.68	4.99
CHO	-45.91	-40.26	4.97

[a] INDO/S'. [b] Vertical tautomers.

Visible-band B values calculated from both INDO/S' and INDO/S are presented for comparison in Table IIIa. The correspondence in both sign and magnitude between the INDO/S' values and the experimental values is quite good. The INDO/S values, on the other hand, are in disagreement with the sign of the experimental values in nearly all cases. This lack of agreement between the experimental and the INDO/S calculated values can be attributed to the relative magnitudes of the frontier orbital energy difference, ΔHOMO and ΔLUMO, calculated from INDO/S (Table IV in ref 17). The INDO/S' parameterization corrects the overestimation of ΔHOMO relative to ΔLUMO that occurs in INDO/S by increasing the importance of resonance interactions between carbon atoms relative to carbon–nitrogen interactions. This decreases the value of the quantity ΔHOMO − ΔLUMO in two ways: first, the b_2 orbital is lowered relative to the b_1 orbital (Figure 7), giving a smaller ΔHOMO; and second, the $\pm E$ influence of the substituents is increased, which tends to both decrease ΔHOMO and increase ΔLUMO in the case of an electron-withdrawing substituent.

McHugh et al.[38] computed the MCD of various D_{4h} and free-base porphyrins, within the PPP approximation, but were unable to correctly predict the sign of visible band MCD in porphine free base. This failure can probably be attributed to the choice of resonance integral parametrization, on the basis of the above finding that the choice of β_{CN}^{π} values relative to the β_{CC}^{π} values has a strong influence on the sign of the calculated B values. Another PPP study[39] computed the Q and Soret band MCD of a formyl-substituted porphyrin and found agreement with the observed sign (inverted) of the MCD of low-spin iron(II) heme a.

In general, the sign and magnitude of MCD calculated for π-substituted porphyrins will be unusually sensitive to the choice of parameters in semiempirical methods, due to the accidental nature of the near-degeneracy of the HOMO's of the parent system, D_{4h} porphine, as well as due to the diluted influence of conjugative substituents. A small variation in orbital energies that would leave the size ranking of the orbital splittings, ΔHOMO and ΔLUMO, unchanged in a smaller π-system, e.g., an adenine,[40] could suffice to invert the order of the orbital energy differences in a porphyrin.

The dominant contribution to the MCD of the visible electronic bands comes from the magnetic-field-induced mixing of the Q_0^x and Q_0^y states (Table IV). The magnitude of the matrix element for this coupling, which corresponds to $|\mu^+|$ of the perimeter model,[19a] is large and nearly constant, with a slight tendency to decrease with increasing electron withdrawal from the ring: $|\langle Q_0^x|\mu|Q_0^y\rangle|$ varies from 5.19 β_e for free-base porphine to 4.97 β_e for formylporphyrin (Table IV). An approximate experimental comparison can be obtained from the spectral data for OEP, where symmetry assures orthogonal polarization of the Q_0^x and Q_0^y bands. Using the Q_0^x B value and Q_0^x and Q_0^y transition moments and energies from Table I, retaining only the term in eq 1 corresponding to Q_0^x–Q_0^y coupling, and solving for the magnetic moment yields a value of 3.3 β_e. This is in reasonable agreement.[41]

Central Proton Tautomerism. Only trans tautomers were considered in the present study,[42] although cis tautomers may need to be considered in very highly perturbed free-base porphyrins, e.g., porphyrins with multiple π-substituents. A recent INDO/S–CI calculation of the electron spectra of the cis and trans tautomers of free-base porphine found the predicted absorption spectra to be almost indistinguishable.[43] It is interesting to note, however, that the reported MO energies correspond, in the context of the Michl model,[19] with normal and inverted MCD for the trans and cis tautomers, respectively. Thus, even though the ordinary absorption spectra are inconclusive on this question, the normal MCD spectrum observed for porphine free base indicates that the trans tautomer is most stable, a conclusion previously reached by less direct routes.[44]

The B values associated with the Q_0^x band calculated for the vertical tautomers vary from $+55 \times 10^{-4}$ $\beta_e \cdot D^2/cm^{-1}$ for vinyl-DAP to -40×10^{-4} $\beta_e \cdot D^2/cm^{-1}$ for formyl-DAP. The calculated sign pattern closely parallels the sign variation experimentally observed for the DMP–X series, in which vertical tautomers are expected to dominate the tautomer distribution (vide supra). Indeed, the only disagreement between the sign predicted for the low-energy electronic bands of the vertical tautomers and the sign pattern observed in the DMP series occurs for the Q_0^y band (III) of the oxime porphyrin. The prediction of identical signs for bands I and III in this compound is unusual, is not observed experimentally, and can be attributed to overestimation of magnetically induced coupling between the Q_0^y and a Soret state. The Soret coupling also adds to the Q_x–Q_y coupling in the compounds with substituents of greater perturbation strength to give excessively large MCD predictions for band III.

The variability of MCD signature predicted for the vertical tautomers contrasts with the situation for the horizontal tautomers, which are all predicted to have positive Q_0^x and B terms and corresponding Q_0^y B terms of opposite sign and nearly equal magnitude. The predictions for the horizontal tautomers accord with experiment only in the case of vinylporphyrin, where, due to the electron-donating character of the vinyl substituent, the horizontal tautomer is indeed expected to be energetically favored.

Temperature Dependence of MCD. The temperature dependence of the MCD associated with the Q_0^x transition in the demethylporphyrins (Table V) provides additional evidence for the presence of tautomeric equilibria. This is particularly clear for the sterically unhindered cyanoporphyrin and the less hindered formylporphyrin, although the similarity of the temperature shift in MCD for all of the strongly perturbing substituents suggests, but does not prove, that a similar mechanism is responsible. Because rotation of carbonyl substituents is expected to induce no larger a change in the MCD of the porphyrin chromophore than does tautomerism,[45] and the energy difference between conformers is expected to be much larger than the central-proton tautomerism energy, the observed temperature dependence is attributed to the latter equilibrium. There is an increase in $B(Q_0^x)$ of 6.53 and 6.76×10^{-4} $\beta_e \cdot D^2/cm^{-1}$ in **2c** and **2g**, respectively, upon raising the temperature from 199 to 295 K. If one assumes

(38) McHugh, A. J.; Gouterman, M.; Weiss, C. *Theor. Chim. Acta* **1972**, *24*, 346–370.
(39) Kaito, A.; Nozawa, T.; Yamamoto, T.; Hatano, M.; Orii, Y. *Chem. Phys. Lett.* **1977**, *52*, 154–160.
(40) For example, INDO/S and INDO/S', two parameterizations employed in this paper, both correctly predict the signs of the three lowest transitions in 9-methyladenine and 9-methyl-8-azadenine (unpublished results of R. A. Goldbeck).
(41) Löwdin deorthogonalization of the AO basis used in the calculations will not significantly affect the sign or magnitude computed for such large moments. (It is expected, on the other hand, to be crucial in computing the sign and magnitude of the much smaller magnetic moments [μ^-] associated with magnetically induced coupling between the Soret states.) See ref 19a for a discussion of Löwdin deorthogonalization and computation of magnetic moments in annulenes.
(42) The X-ray structure of crystalline 4,8-diformyl-2,6-di-*n*-pentyl-1,3,5,7-tetramethylporphin shows the N–H protons in the "vertical" trans arrangement: Chang, C. K.; Hatada, M. H.; Tulinsky, A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 371.
(43) Rawlings, D. C.; Davidson, E. R.; Gouterman, M. *Theor. Chim. Acta (Berlin)* **1982**, *61*, 227–241.
(44) The application of MCD spectroscopy to the determination of protonation sites in heterocycles has recently been explored for a series of azaindolizines: Downing, J. W.; Waluk, J. W.; Stanovnik, B.; Tisler, M.; Vercek, B.; Michl, J. *J. Org. Chem.* **1985**, *50*, 302–311.
(45) See Figure 9 in ref 17 and accompanying discussion.

Table V. MCD and Absorption Spectral Data for Band I of Monosubstituted Demethyl Free Base Porphyrins in Dichloromethane at 295 and 199 K

compound[a]	temp (K)	absorption[b] $\lambda_{max}(10^{-3}\epsilon)/D^c$	absorption[b] $\Delta D/\%$	MCD[b] λ_{max} ($[\theta]_M$)/$10^4 B^d$	MCD[b] $\Delta B/\%$
DMP—CH=CH_2 (**2b**)	295	628 (3.6)/0.93		626 (−1.8)/14.21	
	199	626 (4.0)/0.88	−0.5/−5	623 (−1.8)/14.15	−0.06/−0.4
DMP-$COCH_3$ (**2f**)	295	633 (2.2)/0.66		630 (2.2)/−17.95	
	199	630 (1.9)/0.55	−0.11/−17	628 (3.7)/−25.00	−7.05/−39
DMP-CN (**2c**)	295	624 (1.4)/0.40		623 (2.6)/−21.12	
	199	621 (1.9)/0.43	+0.03/+8	621 (3.8)/−27.50	−6.38/−30
DMP-CHO (**2g**)	295	634 (2.2)/0.69		632 (2.7)/−22.98	
	199	633 (2.4)/0.73	+0.04/+6	630 (4.3)/−29.74	−6.76/−29

[a] Structures are given in Figure 1. [b] A factor of 1.15 has been used to allow for the decrease in volume of CH_2Cl_2 at 199 K. Units of measurement are given in footnotes *c* and *e* of Table I. [c] Values for the dipole strength, *D*, were extracted by a full-band curve-fitting protocol, as in Table I. [d] *B* values were obtained from the zeroth moment, as were band I *B* values in Table I.

that this temperature dependence is entirely due to the equilibrium between two tautomeric forms, vertical and horizontal, then (1) the increase toward positive *B* value with increasing temperature implies that the horizontal tautomers, presumably the higher energy structure, have more positive *B* values than the vertical tautomers, and (2) a consideration of the possible values of the ratio $[B(295\text{ K}) - B(199\text{ K})]/(B_H^0 - B_V^0)$ indicates that the minimum value of $B_H^0 - B_V^0$, the difference between Q_0^x-band *B* values of horizontal and vertical tautomers, that is consistent with the temperature data for **2c,g** is $80 \times 10^{-4}\ \beta_e \cdot D^2/cm^{-1}$ (this is of the order predicted by the calculations, $40\text{–}70 \times 10^{-4}\ \beta_e \cdot D^2/cm^{-1}$).[46] Although the enthalpy difference between tautomers cannot be closely determined from data for these two temperatures, the data for the demethylporphyrins with strong $+E$ substituents suggests that ΔE is probably close to the value that maximizes the above ratio, ca. 0.7 kcal mol^{-1} (Figure 9).

The tautomeric equilibrium is sensitive to the presence of the methyl group adjacent to the π-substituent in the DMP series, as can be seen from a comparison with the temperature data for Q_0^x band MCD in the P series (Table III in ref 17). The *B* values increased by 5.72 and $5.36 \times 10^{-4}\ \beta_e \cdot D^2/cm^{-1}$ for cyano and formyl, respectively, upon going from 199 to 295 K. This is approximately 15% smaller than the temperature dependence found for cyano- and formylporphyrin in the DMP series, and it suggests that either the enthalpy difference between tautomers in the P series porphyrins with strong electron-withdrawing substituents is reduced by several tenths of a kcal/mol from their values in the corresponding DMP series porphyrins, as has already been suggested by the discussion of Figure 8, or that $B_H^0 - B_V^0$ is smaller in **1c** and **1g** than in **2c** and **2g**. The latter, however, is not expected to be a first-order effect.[47]

The temperature data of Table V and the correlations in Figure 8 provide independent evidence for the influence of trans tautomer equilibria on the observed Q_0^x-band MCD of the porphyrin free bases with strongly perturbing π-substituents. Both lines of evidence converge on the order of magnitude and direction for this effect. Figure 8 shows an additional lowering of the formylporphyrin *B* value of about $7 \times 10^{-4}\ \beta_e \cdot D^2/cm^{-1}$. This cannot be accounted for by the direct methyl effect (simple translation of regression lines), while the tautomerism energies derived from the temperature data for DMP–CHO and P–CHO predict that the methyl-induced tautomer shift will lower the DMP–CHO *B* value by $9 \times 10^{-4}\ \beta_e \cdot D^2/cm^{-1}$ at 295 K. The comparison for cyanoporphyrin is also reasonably close: shifts of 12 and 6×10^{-4} $\beta_e \cdot D^2/cm^{-1}$ are obtained from Figure 8 and the temperature data, respectively.[48]

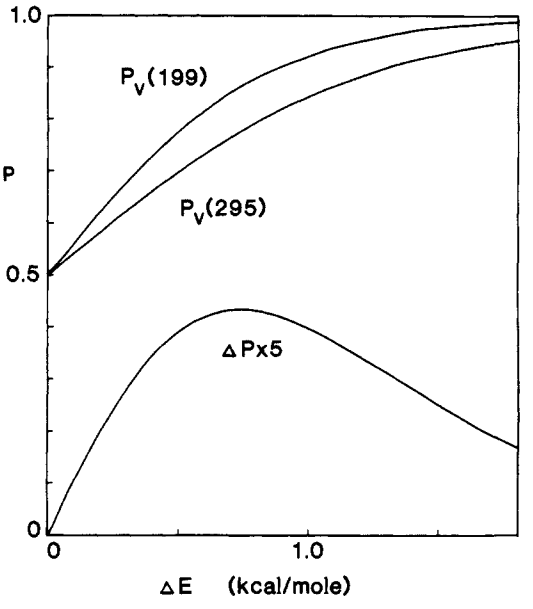

Figure 9. Plot of fractional population of vertical tautomer, P_V, at 199 and 295 K, and $\Delta P = P_V(199) - P_V(295)$, vs. relative stability of vertical and horizontal tautomer, ΔE (see ref 46).

When structural effects of tautomerism and substituent conformation are taken into account, the agreement between measured Q_0^x *B* values and the calculated values is seen to be excellent for all of the DMP compounds except the cyano and vinyl derivatives, for which the magnitudes remain underestimated and overestimated, respectively.[49] Experimental measures of perturbation strength such as spectral shifts,[50] the σ_R^-(g) parameters of Taft,[51] and comparisons with the MCD of substituted benzenes (Figure 8) also rank cyano as a π-perturber of weaker strength than is indicated by the Q_0^x MCD observed in cyanoporphyrins. The latter two effects can be attributed to the high inductive strength of the cyano group, which tends to minimize its effect on the MCD of soft and double-soft chromophores, e.g., benzene.[21b] The ov-

(46) If two tautomeric species, V and H, are in equilibrium and H is less stable than V by ΔE (neglect entropy changes), then the fractional population of V as a function of temperature, $P_V(T)$, is simply given by $(1 + \exp(-\Delta E/RT))^{-1}$. If the observed *B* value associated with an electronic transition is the sum of contributions from V and H, $B_{obsd}(T) = B_V^0 P_V(T) + B_H^0 P_H(T)$, then the difference between B_{obsd} at two temperatures, $\Delta B(T_0,T_1)$, is given by $\Delta B/(B_H^0 - B_V^0) = \Delta P(T_0,T_1,\Delta E) = [P_V(T_0) - P_V(T_1)]$. Inspection of the form of ΔP for T_0 = 199 K and T_1 = 295 K (Figure 12) shows that the maximum possible value of $\Delta B/(B_H^0 - B_V^0)$ is ca. 0.087, which corresponds to ΔE = 750 cal mol^{-1}.

(47) While this applies to the formyl and cyano substituents, out-of-plane conformers of carbonyl-substituted porphyrin free bases will have smaller $B_H^0 - B_V^0$ values than planar conformers.

(48) The minimum physical value of $B_H^0 - B_V^0$ is assumed in obtaining ΔE from Figure 12, 74 and $78 \times 10^{-4}\ \beta_e \cdot D^2/cm^{-1}$ for cyano- and formylporphyrins, respectively. The analysis is not critically sensitive to varying this parameter above its minimum value. For example, a value of $100 \times 10^{-4}\ \beta_e \cdot D^2/cm^{-1}$ yields a predicted shift of $5 \times 10^{-4}\ \beta_e \cdot D^2/cm^{-1}$ for the formyl porphyrins.

(49) An important caveat to keep in mind when making comparisons with quantities from the calculations in the present study, which used planar geometries, is the possible effect of rotated substituent conformers. In particular, the presence of rotated conformers would tend to reorder the other π-acceptor substituents in effective strength relative to the cyano group.

(50) See Figure 6 in ref 17.

(51) (a) Fujio, M.; McIver, R. T.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017–4029. (b) Reynolds, W. F.; Dais, P.; MacIntyre, D. W.; Topson, R. D.; Marriott, S.; Nagy-Felsobuki, E. V.; Taft, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 378–384.

erestimation of vinylporphyrin MCD is the result of overestimation of ΔHOMO (Figure 7).

Tautomerism and Spectral Energies. Implicit in the analysis of MCD for tautomeric effects has been the assumption that shifts in spectral energies accompanying tautomerism are negligible, i.e., much smaller than spectral bandwidths, which are of the order of 500 cm^{-1} and larger. This is at least consistent with the small difference in ground-state energies found above and is also consistent with the small shifts in spectral transition energies predicted by the calculations (horizontal tautomers slightly red-shifted from vertical tautomers). Experimental evidence for tautomer spectral shifts can now be inferred from Table II. The data for cyano- and formylporphyrins suggest an order-of-magnitude estimate of 100 cm^{-1} for the tautomer spectral shift, which is in general agreement with previous findings for free-base porphyrins.[52] The spectral shifts observed for the other π-substituents in Table II are expected to contain, on the basis of the explanation of structural effects presented, appreciable contributions due to perturbation of substituent conformation that will obscure the tautomer-induced shifts.

Conclusions

The data from this study of the visible band MCD of porphyrin free bases with single π-substituents, including vinyl, oxime, cyano, ethoxycarbonyl, acetyl, and formyl substituents, and with alkyl groups at all peripheral pyrrole carbons except that adjacent to the substituent, have enabled us to largely disentangle the conjunctive effects of central-proton tautomerism and substituent conformation that are present and to estimate their separate contributions to the observed MCD. The energy of tautomerism of a strongly perturbed alkyl porphyrin, e.g., formylporphyrin **2g**, has been found to be of the order of 1 kcal mol^{-1}, which is small enough that both trans tautomers will make appreciable contributions to the ambient temperature MCD. When this equilibrium is taken into account, the agreement between observed MCD and the INDO/S′ calculations is found to be generally very good. More temperature data are clearly needed to determine $B_H^0 - B_V^0$ and the tautomerism energies, and such work is in progress.

The small size and the direction of the spectral energy shifts due to tautomerism found in the present study allow us to discount the previously raised possibility[17] that the bisignate MCD observed in the acetyl porphyrin **1f** and cyanoporphyrin **1c** was due to shifted contributions of trans tautomers. The alternative hypothesis advanced for P-$COCH_3$ attributes the bisignate MCD to the presence of comparable populations of rotated and nearly planar conformers.[17] This hypothesis is consistent with the pattern of substituent effects on MCD found in the present study, as well as with the magnitude and direction of the spectral energy shifts observed.

More information about substituent effects can be obtained from study of the MCD of series of porphyrins containing more finely graded steric interactions, porphyrins containing metals as the central substituent, and porphyrins with π-substituents that are constrained by the σ-framework to known geometries. Work along these lines, with recently synthesized model porphyrins,[53] is in progress.

Synthetic and Analytical Methods

Materials. The syntheses of porphyrins DMP—$CH{=}CH_2$ (**2b**), DMP-CN (**2c**), DMP—$CO_2C_2H_5$ (**2e**), DMP—$COCH_3$ (**2f**), and DMP—CHO (**2g**) have previously been reported.[53] The porphyrins P—H (**1a**) and DMP—H (**2a**) were synthesized from the copper complexes of the acetylporphyrins **1f** and **2f**, respectively, by treatment with ethanedithiol according to a method described by Smith et al.[54] followed by demetalation.[55] The porphyrin oximes (*E*)-P—CH=NOH (**1d**) and (*E*)-DMP—CH=NOH (**2d**) were prepared from the corresponding aldehydes **1g** and **2g**, respectively, by reaction with hydroxylamine hydrochloride in pyridine. A mixture of the *E*- and *Z*-oxime was found in the reaction of DMP—CHO (**2g**). The isomers were subsequently separated by repeated column chromatography (silica gel, $CHCl_3$:MeOH 95:5 as eluent). The less polar porphyrin oxime was assigned the *E* configuration and the more polar and less abundant the *Z* configuration. The crucial evidence for the stereochemical assignment was obtained from the MCD of each isomer. The *Z* isomer adopts, as a result of increased steric interaction, a more twisted conformation compared to the *E* isomer which is allowed to become more planar with respect to the porphyrin ring. Consequently, the *Z* isomer exhibits a more positive *B* value for the Q_0^x transition in the MCD than does the *E* isomer. This illustrates in a demonstrative way the utility of MCD in structure elucidation. The same information is not accessible from the absorption spectra, which are virtually identical for the *Z* and *E* isomers.

Analytical Procedures. Melting points were measured with a Thomas Hoover capillary melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a 300-MHz Nicolet NT300WB instrument in $CDCl_3$ with the solvent peak ($CHCl_3$) as internal standard or in CF_3CO_2D with tetramethylsilane as internal standard. Mass spectra were obtained on a Ribermag R10-10C quadrupole mass spectrometer. Elemental analyses were obtained from the microanalytical laboratories at Stanford and Berkeley. Neutral alumina (Fischer) activity grade III and silica gel 60 (Merck) were used for column chromatography. The purity of each porphyrin was monitored by analytical TLC (Merck silica gel 60 F254).

3,7,13-Tris(2-methoxycarbonylethyl)-2,8,12,17-tetramethyl-[21*H*,23*H*]porphine (1a): yield 53%; mp 202–203 °C (CH_2Cl_2–CH_3OH); ^1H NMR (300 MHz, $CDCl_3$) δ 3.259–3.322 (m, 6 H, $CH_2CH_2CO_2Me$), 3.643 (s, 3 H)8 3.653 (s, 3 H), 3.659 (s, 6 H), 3.670 (s, 3 H), 3.678 (s, 3 H), 3.766 (d, 3 H, *J* = 0.9 Hz) (Ar CH_3 and CO_2CH_3), 4.436 (t, 6 H, *J* = 7.8 Hz, $CH_2CH_2CO_2Me$), 9.106 (d, 1 H, *J* = 0.8 Hz, Ar H), 10.051 (s, 1 H), 10.109 (s, 1 H), 10.125 (s, 1 H), 10.132 (s, 1 H) (methine protons).

Anal. Calcd for $C_{36}H_{40}N_4O_6$: C, 69.21; H, 6.45; N, 8.97. Found: C, 69.02; H, 6.39; N, 8.69.

8-Hydroximino-3,13,17-tris(2-(methoxycarbonyl)ethyl)-2,7,12,18-tetramethyl[21*H*,23*H*]porphine (1d): yield 76%; mp 238–239 °C (CH_3OHCH_3Cl); ^1H NMR (300 MHz, CF_3CO_2D) δ 3.33 (m, 6 H, 3 × Ar $CH_2CH_2CO_2Me$), 3.80, 3.83, 3.85, 4.02 (18 H, 3 × Ar CH_3, 3 × CO_2CH_3), 4.11 (s, 3 H, Ar CH_3), 4.72 (m, 6 H, Ar $CH_2CH_2CO_2Me$), 10.11 (s, 1 H), 11.01 (s, 1 H), 11.17 (s, 1 H), 11.22 (s, 1 H), 11.84 (s, 1 H) (methine protons and C*H*=NOH).

Anal. Calcd for $C_{37}H_{41}N_5O_7$: C, 66.54; H, 6.19; N, 10.49. Found: C, 66.72; H, 6.32; N, 10.48.

3,7,13-Tris(2-(methoxycarbonyl)ethyl)-2,8,12-trimethyl[21*H*,23*H*]-porphine (2a): yield 24%; mp 199–200 °C (CH_2Cl_2–CH_3OH); ^1H NMR (300 MHz, $CDCl_3$) δ 3.298 (m, 6 H, $CH_2CH_2CO_2Me$), 3.652 (s, 9 H, 3 × CO_2CH_3), 3.682 (s, 3 H, Ar CH_3), 3.688 (s, 3 H, Ar CH_3), 3.715 (s, 3 H, Ar CH_3), 4.444 (m, 6 H, $CH_2CH_2CO_2Me$), 9.416 (s, 2 H, 2 × $^{\beta}H$), 10.135 (s, 2 H), 10.165 (s, 1 H), 10.196 (s, 1 H) (4 × methine H).

Anal. Calcd for $C_{35}H_{38}N_4O_6$: C, 68.84; H, 6.27; N, 9.17. Found: C, 68.60; H, 6.17; N, 9.08.

8-(*E*)-Hydroximino-3,13,17-tris[(2-methoxycarbonyl)ethyl]-2,12,18-trimethyl[21H,23H]porphine (2d): mp 223–224 °C (CH_3Cl–CH_3OH); ^1H NMR (300 MHz, $CDCl_3$) δ 3.272 (t, 6 H, *J* = 7.7 Hz, 3 × $CH_2CH_2CO_2Me$), 3.583, 3.629, 3.636, 3.665, 3.699 (s, 18 H, 3 × Ar CH_3, 3 × CO_2CH_3), 4.348 (t, 2 H, *J* = 7.7 Hz, $CH_2CH_2CO_2Me$), 4.413 (t, 4 H, *J* = 7.6 Hz, $CH_2CH_2CO_2Me$), 7.81 (s, 1 H, CH=NO*H*), 9.410 (s, 1 H), 9.546 (s, 1 H), 10.015 (s, 3 H), 10.751 (s, 1 H) (methine protons, $^{\beta}H$ and C*H*=NOH).

Anal. Calcd for $C_{36}N_{39}N_5O_7$: C, 66.14; H, 6.02; N, 10.71. Found: C, 65.92; H, 5.84; N, 10.39.

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Registry No. 1a, 62786-94-1; **1d**, 103884-74-8; **2a**, 103884-75-9; **2b**, 91238-15-2; **2c**, 91238-17-4; (*E*)-**2d**, 103884-76-0; (*Z*)-**2d**, 103884-77-1; **2e**, 103884-78-2; **2f**, 91238-14-1; **2g**, 91238-16-3.

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