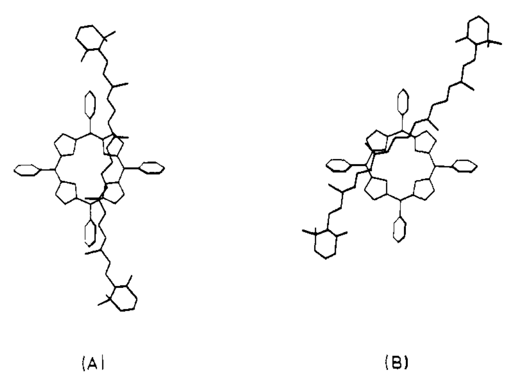

Figure 7. Association of TPP–β-carotene: preferred conformations of type A and B. For A, $\Delta l_{\perp} = 0$, $\Delta l_{\parallel} = 2$ Å, $E_{\min} = -13.8$ kcal·mol^{-1}, $z = 3.6$ Å. For B, $\Delta l_{\perp} = 2$ Å, $\Delta l_{\parallel} = 2$ Å, $E_{\min} = -12.9$ kcal·mol^{-1}, $z = 4.2$ Å.

this study can contribute to the interpretation of some details.

Although the ortho ester molecule is not perfectly rigid the mean conformation is tightly folded with porphyrin and carotenoid planes parallel and separated by 3.6–4 Å. This is related to the large energy transfer rate constant, similar in polystyrene matrix ($k \geq 1.3 \times 10^8$ s^{-1}) and in solution ($k \geq 2 \times 10^8$ s^{-1}).

Owing to the rather broad energy minima, the ortho ether conformations range from folded to partly extended. In solution the carotenoid chain can move over the porphyrin cycle, but the π-orbital overlap is less efficient than for the ortho ester, leading to a slightly smaller rate constant (10^8 s^{-1}). The probability of stacked conformations can be estimated from the energy curves (Figure 5) as ~400 times smaller than for the ortho ester (the probability is proportional to $\Delta q \exp(-U/RT)$ where Δq and U are the width and the depth of the energy minimum). This is consistent with the slow decay rate ($k = 4.4 \times 10^6$ s^{-1}) obtained in a plastic matrix which prevents any molecular motion. The energy transfer therefore has been assumed to occur across the covalent linkage.

The geometrical constraints of the covalent linkage in the ortho ester lead to very efficient conformations for both triplet and singlet energy transfer. It is noteworthy that their characteristics (distance of the parallel planes, stability) are very similar to those of the free association porphyrin–β-carotene or TPP–β-carotene which depend only on the interaction between the two parts. Such arrangements associate photophysical properties and stability; they can also be expected in photosynthetic membranes for chlorophyll and carotenoid pigments, which lack covalent linkages, although these molecules are submitted to other constraints by their environment. Recently[27] a non-covalently linked stacked dimer of two bacteriochlorophyl b (distance ~3 Å) has been found in the photosynthetic reaction center of a purple bacterium.

Acknowledgment. We are indebted to R. Bensasson for suggesting this study and continuous interest. We are very grateful to D. Gust for having compared our predicted configurations against NMR experimental results and for his helpful critical reading of our manuscript. We also thank C. Chachaty for providing us details on the conformations deduced from NMR spectra. The computations have been performed at the Centre Inter Regional de Calcul Electronique that we thank for its technical assistance.

Registry No. TPP, 917-23-7; TPP-*o*-CO_2CH_2-*p*-$C_6H_4CH{=}CHC(CH_3){=}CHCH{=}CHCH(CH_3){=}CHCH{=}CHCH{=}C(CH_3)CH{=}CHCH{=}C(CH_3)CH{=}CHC{=}C(Me)(CH_2)_3C(Me)_2$, 105230-66-8; TPP-*o*-$CH_2$-*p*-$C_6H_4CH{=}CHC(CH_3){=}CHCH{=}CHCH(CH_3){=}CHCH{=}CHCH{=}C(CH_3)CH{=}CHCH{=}C(CH_3)CH{=}CHC{=}C(Me)(CH_2)_3C(Me)_2$, 105230-67-9; TPP-*o*-$CO_2CH_2$-*p*-$C_6H_4CH{=}CHC(CH_3){=}CHCH{=}CHC(CH_3){=}CHCH{=}CH_2$, 105230-68-0; TPP-*o*-$OCH_2$-*p*-$C_6H_4CH{=}CHC(CH_3){=}CHCH{=}CHC(CH_3){=}CHCH{=}CH_2$, 105230-69-1; β-carotene, 7235-40-7.

---

(27) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385–398.

Substituent Conformational Effects in the Magnetic Circular Dichroism and Absorption Spectra of Free-Base Carbonyl Porphyrins[1]

Robert A. Goldbeck,* Bo-Ragnar Tolf,[2a] Edward Bunnenberg,[2b] and Carl Djerassi*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received June 23, 1986*

Abstract: Our previous MCD and absorption spectral studies of monosubstituted free-base alkylporphyrins found evidence in the sign and magnitude of visible-band MCD for out-of-plane conformers of π substituents, as well as effects due to the electronic influence of alkyl groups and the equilibrium of central-proton tautomers. The present study examines the MCD and absorption spectra of a series of acetylheptaalkylporphyrin free bases with various alkyl groups adjacent to the acetyl, as well as a fused-ring ketocyclohexenoporphyrin. Out-of-plane rotation angles of approximately 85, 65, and 35° for the acetyl moiety of the *tert*-butyl-, isopropyl-, and ethyl-substituted porphyrins, respectively, are deduced from variations in the observed MCD of the $Q_0{}^x$ band. INDO calculations of B terms for acetylporphyrin free base are found to reproduce the angle dependence observed for the MCD.

The occurrence of sign inversion in the magnetic circular dichroism (MCD) spectroscopy of two series of monosubstituted free-base porphyrins was recently studied.[3,4] The structures of these two series, **1** and **2**, are quite similar. As shown in Figure 1, series **2** is formally obtained from **1** by removal of the methyl adjacent to the π substituent, yet their MCD showed significant

---

[1] Part 68 in the series "Magnetic Circular Dichroism Studies". For part 67, see ref 4b.

[2] (a) Present address: Pharmacia AB, S-751 82 Uppsala, Sweden. (b) Deceased December 8, 1984.

[3] Lu, Y.; Shu, A. Y. L.; Knierzinger, A.; Clezy, P. S.; Bunnenberg, E.; Djerassi, C. *Tetrahedron Lett.* **1983**, *24*, 2433.

[4] (a) Djerassi, C.; Lu, Y.; Waleh, A.; Shu, A. Y. L.; Goldbeck, R. A.; Kehres, L. A.; Crandell, C. W.; Wee, A. G. H.; Knierzinger, A.; Gaete-Holmes, R.; Loew, G. H.; Clezy, P. S.; Bunnenberg, E. *J. Am. Chem. Soc.* **1984**, *106*, 4241–4258. (b) Goldbeck, R. A.; Tolf, B.-R.; Wee, A. G. H.; Shu, A. Y. L.; Bunnenberg, E.; Djerassi, C. *Ibid.*, in press.

0002-7863/87/1509-0028$01.50/0

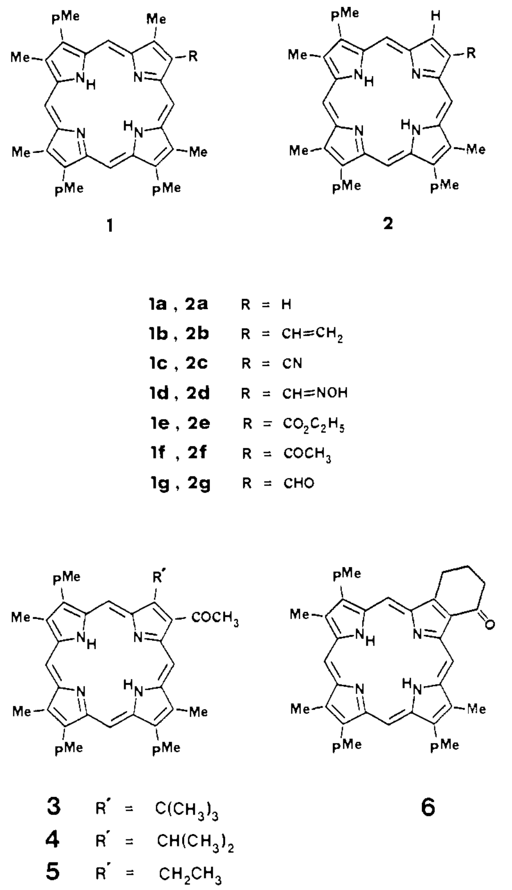

Figure 1. Structures of monosubstituted free-base porphyrins. Central protons are depicted in the "vertical" orientation. Me = methyl; p = propionate.

differences. In the MCD spectra of the ethoxycarbonyl porphyrins (**1e**, **2e**), for example, the sign pattern of the ellipticity of the Q_0^x and Q_0^y electronic bands was "normal" (sign pattern of $[\theta]_M$ is −+ with increasing energy) in the methyl compound and strongly inverted in the demethyl homologue.[4b] It is well-established that an electron-withdrawing group of sufficient strength, e.g., formyl, can induce a reversal in the sign of the MCD of the visible electronic bands in porphyrins. Evidently the electron-withdrawing effect of the π substituent was reduced or masked in the methyl porphyrins (series **1**). Simple perturbation considerations, as well as explicit INDO calculations, indicated that out-of-plane conformers of carbonyl porphyrins will have more positive B values associated with the Q_0^x band[5] than in-plane conformers. At the same time, the strong effect of central proton tautomerism on MCD required that this equilibrium also be taken into account. The less stable "horizontal" trans tautomers (substituted pyrrole protonated) can have considerably more positive Q_0^x band B values than the lower energy "vertical" tautomers. Furthermore, the number of alkyl groups on the porphyrin ring is known to also affect MCD and absorption spectral intensities. Variations in MCD spectra between the two series were thus found to arise from three sources: (1) the direct electronic effect of the adjacent methyl group (modest electron donor) on π-MO energies and thus on MCD; (2) steric modulation of the direct electronic effect on MCD of the π substituent; and (3) shifts in the equilibrium between the trans N–H tautomers correlated with the first two effects.

The question of substituent conformation and its influence on MCD sign and magnitude is important in order to establish a connection between the response of the porphyrin π system to substitution and the large body of empirical correlations that have been established for smaller aromatics, e.g., substituted benzenes.[6] It is also of biochemical interest since, for instance, modulation of dihedral angle may be an important factor affecting function during the enzymatic cycle of cytochrome *c* oxidase. However, relatively little is known about the conformation of π substituents with respect to the porphyrin ring. The vinyl groups of crystalline protoporphyrin IX dimethyl ester (DME) are known to point 20° out of the porphyrin plane from the adjacent methyl.[7] The ^{1}H NMR of biscyano iron(III) protoporphyrin IX DME[8] and heme[9] are also consistent with out-of-plane vinyl conformers, as is the resonance Raman of heme.[10] In crystalline nickel(II) 2,4-diacetyldeuteroporphyrin IX DME, the acetyls are found to be 3 and 17° out-of-plane from the meso hydrogen,[11] consistent with the ^{13}C NMR of the free base.[12] The carbonyl moieties were found to be more nearly coplanar, ca. 5°, in a crystalline diformylporphyrin.[13]

In order to provide further experimental information on the question of substituent conformation, we now report the MCD and absorption spectra of a series of carbonyl-substituted porphyrin free bases with a range of steric encumbrances influencing the carbonyl orientation. Substituent conformation was found to play a role in influencing the MCD of the porphyrins in series **1** and **2**,[4] where it probably accounts for most of the variation between formyl, acetyl, and ethoxycarbonyl porphyrins within each series. The electronic effect of methylation of the porphyrin ring and the concomitant shift in tautomer equilibrium, however, were found to exert a comparable influence on visible-band MCD; therefore, the number of alkyl groups peripheral to the porphyrin ring is kept constant in the present study, and the effect of varying the nature of the alkyl group adjacent to the carbonyl substituent is examined.

Methods

The synthetic methods used to obtain porphyrins in the present study are to be presented elsewhere.[14] The ketocyclohexenoporphyrin compound was a gift from P. S. Clezy. MCD and absorption spectral measurements and their analysis are discussed in detail in ref 4a. The INDO/S' method used for calculating B terms has been described previously.[4b] Geometries for the porphyrin ring and substituents were the same as employed earlier.[4a]

Results and Discussion

We consider in this study a series of porphyrins (**3**–**6** in Figure 1) in which one pyrrole ring is adjacently substituted with an acetyl and various alkyl groups, while the peripheral alkyl groups on the remaining pyrrole rings remain unchanged. Of the interfering groups, *tert*-butyl (**3**) is the bulkiest and ethyl (**5**) the smallest. Compound **6** can be formally derived from **5** by covalently linking the acetyl and adjacent ethyl substituent to form a fused cyclohexenone ring.

The MCD and absorption spectra of porphyrins **3**–**6** are overlayed in Figure 2. The spectral parameters extracted from the data are presented in Table I. The visible-band MCD of porphyrin **3** is strongly "normal" (sign pattern of $[\theta]_M$ of electronic

---

(5) The convention for the sign and magnitude of B values employed in our MCD studies is set forth in: Stephens, P. J.; Suetaka, W.; Schatz, P. N. *J. Chem. Phys.* **1966**, *44*, 4592. With the definition, the integrated B value of an isolated band will be opposite in sign to $[\theta]_M$. Some authors have adopted a different convention for Faraday parameters advanced in: Stephens, P. J. *Adv. Chem. Phys.* **1976**, *35*, 197. Conversion between conventions is discussed in: Piepho, S. B.; Schatz, P. N. *Group Theory in Spectroscopy with Applications to MCD*; Wiley-Interscience: New York, 1983; pp 533–540.

(6) Weeks, G. H.; Adcock, W.; Klingensmith, K. A.; Waluk, J. W.; West, R.; Vasak, M.; Downing, J.; Michl, J. *Pure Appl. Chem.* **1986**, *58*, 39–53 and references therein.

(7) Caughey, W. S.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 6639.

(8) LeMar, G. N.; Viscio, D. B.; Gersonde, K.; Sick, H. *Biochemistry* **1978**, *17*, 361.

(9) Satterlee, J. D.; Erman, J. E. *J. Biol. Chem.* **1983**, *258*, 1050.

(10) (a) Rousseau, D. L.; Ondrias, M. R.; LaMar, G. N.; Kong, S. B.; Smith, K. M. *J. Biol. Chem.* **1983**, *258*, 1740. (b) Shelnutt, J. A.; Satterlee, J. D. *Ibid.* **1983**, *258*, 2168.

(11) Hamor, T. A.; Caughey, W. S.; Hoard, J. L. *J. Am. Chem. Soc.* **1965**, *87*, 2305.

(12) Doddrell, D.; Caughey, W. S. *J. Am. Chem. Soc.* **1972**, *94*, 2510.

(13) Chang, C. K.; Hatada, M. H.; Tulinksy, A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 371.

(14) Tolf, B.-R.; Wee, A. G. H.; Shu, A. Y. L.; Bunnenberg, E.; Djerassi, C., to be published.

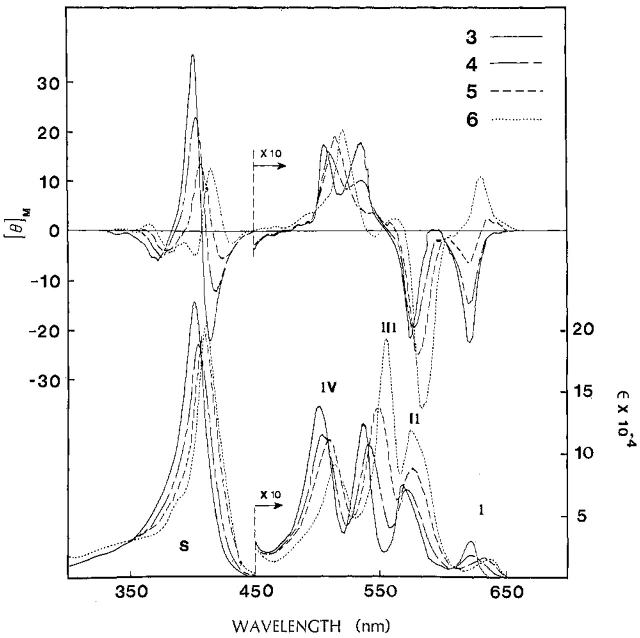

Figure 2. MCD and absorption spectra of 2-*tert*-butyl-3-acetylporphyrin (**3**), 2-isopropyl-3-acetylporphyrin (**4**), 2-ethyl-3-acetylporphyrin (**5**), and ketocyclohexenoporphyrin (**6**) free bases in chloroform. Structures are shown in Figure 1. Concentrations are less than 10^{-4} M.

bands is −+ with increasing energy) and resembles the MCD of the unsubstituted heptaalkylporphine free base (**1a**).[4b] The increasing π-perturbation strength through the series is evidenced by the increasingly positive value of $[\theta]_M$ for band I in the order $-C(CH_3)_3 < -CH(CH_3)_2 < -CH_2CH_3 < -CH_2CH_2-$. The MCD associated with band I of **6** is strongly inverted, with a *B* value that is nearly as negative as that of formylporphyrin **1g**.[4a] The incomplete inversion of MCD sign in band III of **6**, however, is an indication that the π-perturbation is not quite as strong as that found in **1g**.

The decreasing steric bulk of the alkyl substituent in porphyrins **3–5** apparently allows a more coplanar orientation of the adjacent acetyl group, which is reflected in more negative *B* values for band I. The most coplanar orientation should be found in compound **6**, where the carbonyl moiety is constrained to a nearly planar geometry by the σ framework. The MCD of this fused-ring porphyrin establishes that the variation in MCD seen in this series is, in fact, principally due to conformational changes forced by the steric bulk of the alkyl group, rather than variations in the electron-donating propensity of the alkyl substituent. The latter possibility is considered because of the important influence of the direct electronic effect of peripheral alkyl groups on MCD found in previous studies.[4] Nevertheless, the dominant influence on MCD for this series is substituent conformation, as evidence by the band I *B* value ($-6.91 \times 10^{-4}\beta_e D^2/\text{cm}^{-1}$) of compound **6** (Table I), which would be expected to lie between those for **4** ($12.0 \times 10^{-4}\beta_e D^2/\text{cm}^{-1}$) and **5** ($3.6 \times 10^{-4}\beta_e D^2/\text{cm}^{-1}$ [total band I *B* value]) if the electronic character of the alkyl group was the dominant influence.[15] The dramatic differences in visible band MCD seen in Figure 2 are therefore attributed to conformational changes of the acetyl group.

This trend in the MCD parameters is also accompanied by shifts in the transition energies; the Soret and Q_0^x absorption bands of the ketocyclohexenoporphyrin **6** are red shifted by 600 and 430 cm^{-1}, respectively, relative to **3**. The correlation between the shifts in absorption energy and the trend in *B* values for band I through the series (Figure 3) is very linear ($r = 0.9691$). This is in contrast to the dipole strengths (Table I), which show a variation with transition frequency that is not nearly as large or systematic. The plot (Figure 3) of *D* values vs. shifts in absorption energies for band I is more scattered ($r = 0.3220$) and the systematic trend in *D*, indicated by the regression line, shows a rise of less than 10% through the series.

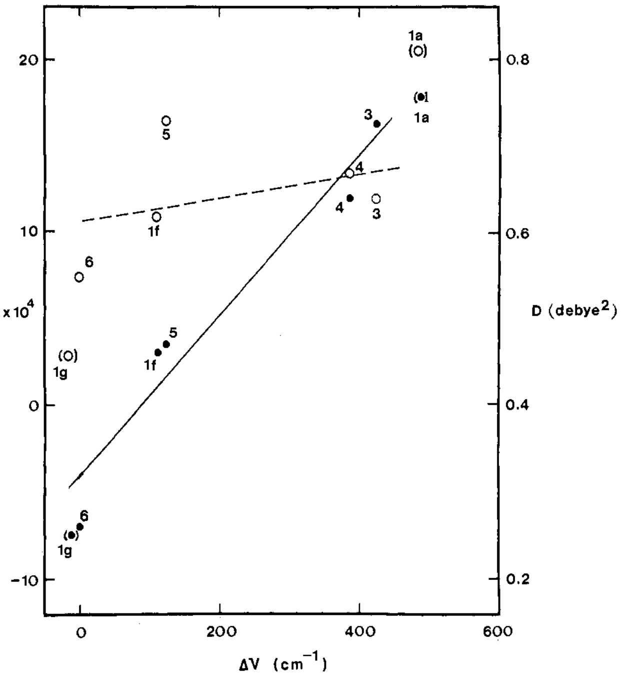

Figure 3. Plot of *B* values (filled circles) and dipole strengths, *D* (open circles) vs. absorption energies for Q_0^x band of free-base acetylporphyrins. Solid and brocken curves are linear regression fits for *B* value ($r = 0.9691$) and dipole strength ($r = 0.3220$) data, respectively (points in parentheses are omitted from fits).

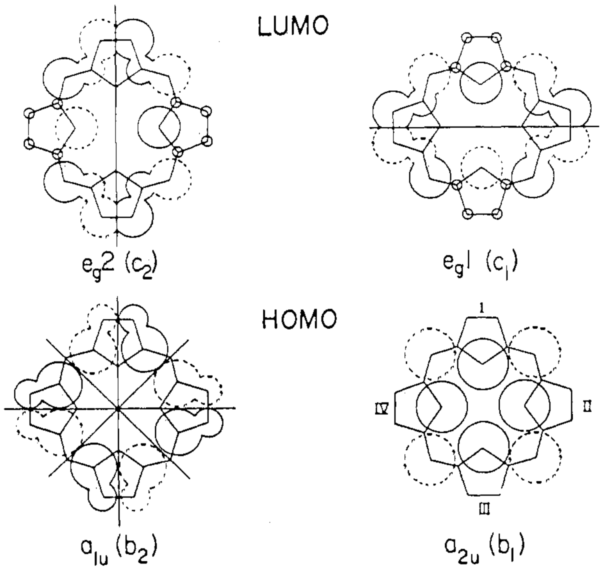

Figure 4. Schematic diagram of porphyrin frontier molecular orbitals (redrawn from ref 16). Symmetry labels refer to the D_{4h} symmetry of the porphine ring.

The proportionality between *B* values and shifts in absorption energies can be explained in terms of the four-orbital model,[16,17] in which changes in both MCD intensity and transition frequencies of the Q_0^x band of the hindered carbonyl porphyrins are proportional to shifts in the energy of the c_1 LUMO, which possesses a large AO coefficient at the carbon bound to the carbonyl (Figure

---

[15] Alkyl groups were in general found to have very similar electron-donating propensities in a study in ref 6 of the MCD of the L_b band of substituted benzenes.

[16] Gouterman, M. *J. Mol. Spectrosc.* **1961**, *6*, 138–163.

[17] (a) Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6801. (*b*) Michl, J. *Ibid.* **1978**, *100*, 6812. (c) Michl, J. *Ibid.* **1978**, *100*, 6819. (d) Michl, J. *Tetrahedron* **1984**, *40*, 3845.

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

		Soret and near-UV region						Q_0^y			Q_0^x	
acetyl-R-porphyrin[b]	spectrum						Q_1^y IV	IIIb	IIIa	Q_1^x II	Ib	Ia
3 ($-C(CH_3)_3$)	MCD[c]			372	401	414	506	536		575	623	
				-6.1	35.5	-21.7	1.7	1.9		-2.1	-2.3	
							-15.4	-20.4		14.0	16.1	
	ABSN[d]				402		502	537		569	622	
					223		13.9	12.4		7.4	3.0	
					126		6.7	3.9		2.7	0.64	
4 ($-CH(CH_3)_2$)	MCD			376	404	420	511	534		577	622	
				-5.3	22.7	-11.9	1.5	1.0		-1.9	-1.5	
							-15.8	-11.6		18.9	12.0	
	ABSN				406		505	541		572	624	
					188		11.6	10.8		7.1	1.8	
					120		6.4	4.8		3.3	0.67	
5 ($-CH_2CH_3$)	MCD			380	408	423	515	546 (s)		581	622	638
				-4.4	13.5	-5.6	1.9	0.4		-2.5	-0.6	0.2
							-23.1	-3.0		25.2	5.20	-1.64
	ABSN				410		510	549		576	635	
					197		11.1	13.8		8.8	1.6	
					117		6.9	6.3		4.0	0.73	
6 ($-CH_2CH_2-$)	MCD	366	385	402	416	433	521	546	565	584	632	
		1.2	-4.0	-5.0	12.6	-2.4	2.0	-0.1	0.2	-3.6	1.1	
							-19.6	0.4	-2.0	33.1	-6.91	
	ABSN				412		515	555		576	639	
					204		9.1	19.2		11.9	1.6	
					110		5.4	6.2		4.9	0.55	

[a] Principal spectral features evident in chloroform solutions. [b] Structures are given in Figure 1. [c] MCD: $\lambda_{max}/[\theta]_M/10^4B$. Wavelength in nanometers: s = shoulder; molar magnetic ellipticity, $[\theta]_M$, in deg cm^2 dmol^{-1} G^{-1}; values of the B term are in D^2 μ_B/cm^{-1}. [d] ABSN: $\lambda_{max}/10^{-3}\epsilon/D$. Wavelength in nanometers; molar extinction coefficient, ϵ, in 1000 cm^2 mol^{-1}; values for the dipole strength, D, are in D^2.

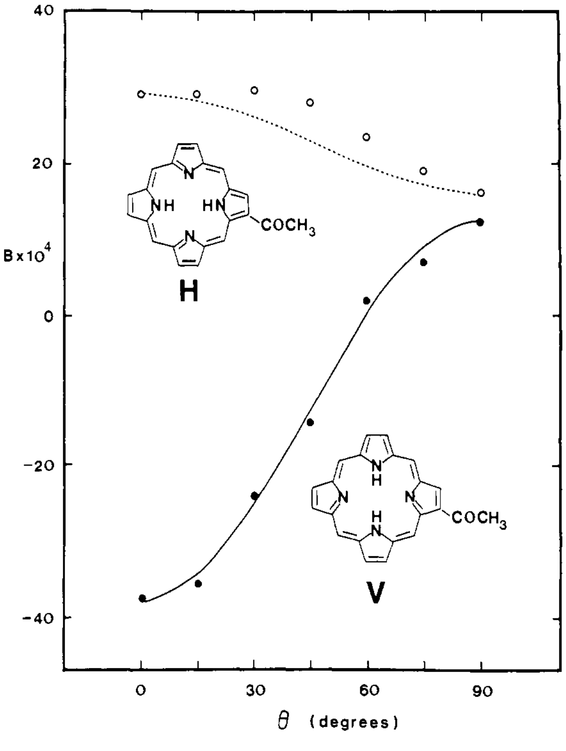

Figure 5. Plot of INDO/S' B values of (H)orizontal and (V)ertical tautomers of acetylporphyrin free base for selected values of the rotation angle of acetyl π system with respect to the plane of the porphyrin ring. Curves represent interpolation between endpoints of a $\cos^2\theta$ dependence.

Table II. INDO/S' Frontier MO Energies (eV) for Rotated Conformers of Acetylporphyrin Free Base

θ (deg)	b_1	b_2	c_1	c_2	θ'^a (deg)
		Vertical Tautomer			
0	-6.570	-6.384	-1.686	-1.259	≡0
15	-6.571	-6.385	-1.680	-1.260	11
30	-6.567	-6.373	-1.642	-1.258	32
45	-6.567	-6.366	-1.611	-1.259	44
60	-6.567	-6.350	-1.563	-1.260	64
75	-6.571	-6.346	-1.541	-1.265	77
90	-6.583	-6.343	-1.533	-1.277	≡90
		Horizontal Tautomer			
0	-6.585	-6.379	-1.588	-1.431	≡0
15	-6.583	-6.379	-1.581	-1.431	9
30	-6.570	-6.365	-1.408	-1.430	50
45	-6.562	-6.356	-1.380	-1.521	55
60	-6.558	-6.358	-1.322	-1.506	68
75	-6.559	-6.332	-1.291	-1.507	78
90	-6.569	-6.335	-1.278	-1.516	≡90

[a] $\arcsin \{[c_1(\theta) - c_1(0°)]/[c_1(90°) - c_1(0°)]\}^{1/2}$.

Table III. Average Rotation Angles of Carbonylporphyrin Conformers Inferred from MCD of Q_0^x Band

compd	R	θ (deg)
3	*tert*-butyl	85 ± 10
4	isopropyl	65 ± 5
5	ethyl	35 ± 5
1f	methyl	35 ± 5
6	cyclohexenone	0 ± 5

4). INDO/S' MO calculations show that this MO energy in the vertical tautomer has the expected cosine squared dependence on the rotation angle, θ, about the acetyl–porphine bond (Table II). B values calculated from INDO/S' CI wave functions for rotated conformers of acetylporphyrin free base also have this trigonometric dependence (cf. Figure 5). A covariation of B value with LUMO energy follows from Michl's perimeter model of MCD,[17] wherein the B value of the lowest energy electronic band is more generally proportional, albeit approximately, to the double energy difference among frontier orbitals ΔHOMO – ΔLUMO. (A level crossing between the LUMO's of the horizontal tautomer causes the angle dependence of the MCD predictions to be smaller than that found in the vertical tautomers, and results in a small deviation from cosine squared dependence.)

The angle dependence of calculated B values suggests that the data may be described approximately by two parameters, a and b: $B(\theta) = a\cos^2\theta + b$. Conformer rotation angles inferred from this fit to the experimental data for the compounds in Figure 3 are shown in Table III. The angles follow the expected trend and rise steeply with increasing steric bulk of the interfering group. The reported uncertainties reflect the degree of arbitrariness in assigning angles to the endpoints, **3** and **6**.[18] The smallest out-

Table IV. $B(\theta) = a \cos^2 \theta + b^a$

	a	b
experiment[b]	−19.7	15.6
INDO/S′[c] ($K_{\text{taut}} = 0.35$)[d]	−33.7	13.4

[a] Units are $10^{-4}\beta_e D^2/\text{cm}^{-1}$. [b] Taken from linear regression in Figure 3. [c] The INDO/S′ values of Figure 5 for vertical and horizontal tautomers are used within the approximation that the mole fraction of horizontal tautomers, f_H, is independent of conformer angle. (Relaxing this approximation introduces an angle dependence in a and b too small to detect in the present study.) [d] See footnote 20.

of-plane rotation angle LUMO's for the free acetyl, 35°, is significantly larger than the values from the crystal structure[11] of diacetylporphyrin.[19]

The magnitude of the change in B value associated with rotation about the carbonyl–porphyrin bond is indicated by the a parameter introduced above. The experimentally derived parameters, a and b, are compared in Table IV with values predicted from the INDO/S' results.[20] The angle dependence predicted from INDO is 50% larger than the observed angle dependence.[21]

Conclusions

The B terms extracted from the $Q_0{}^x$ band MCD of porphyrin derivatives show a sensitivity to structural variations in the chromophore that is both larger and more systematic than that displayed by the comparable integrated quantities in ordinary absorption spectra, the dipole strengths. This sensitivity is most dramatically displayed in the phenomenom of sign inversion, which can be induced in the $Q_0{}^x$ band of porphyrins by electron-withdrawing π substituents, e.g., in porphyrin **6**. Since the occurrence of sign inversion is also strongly modulated by the position of the central protons, the two effects, electron withdrawal by π substituents and central proton tautomerism, are found to act conjunctively to determine the observed MCD.

This structural sensitivity allows the application of empirical correlations and theoretical models, both simple (Michl[17] perimeter model) and sophisticated (INDO), to the measured MCD to yield information about π-substituent conformation and central proton tautomerism. Rotation angles with respect to the planar of the porphyrin ring were deduced in the present study for carbonyl substituents from variations in the $Q_0{}^x$ band MCD. The observed angle dependence of MCD was reproduced reasonably well by INDO calculations using assumptions about the tautomer equilibrium derived from previous MCD[4] and NMR[20] studies.

Acknowledgment. We are indebted to Mrs. Ruth Records for MCD measurements, to Professor Peter S. Clezy for porphyrin samples, and to Dr. Steven J. Milder for comments. Financial support for this work was provided in part by grants from the National Institutes of Health (GM-20276) and the National Science Foundation (CHE 80-25733).

Registry No. **1f**, 63940-11-4; **3**, 105230-12-4; **4**, 105230-13-5; **5**, 105230-14-6; **6**, 105230-15-7.

---

(18) This was established for **3** on the basis of MCD spectral similarities with those of **1a** in ref 4b.

(19) The small C–C distances in ref 11 between acetyl methyls and side chains on neighboring porphyrins suggest that large intermolecular steric interactions present in the solid state could account for this difference.

(20) In order to compare the INDO/S' results for horizontal and vertical tautomers with experiment, a value of the tautomer equilibrium constant must be specified. $K = 0.35$ is consistent with our earlier MCD studies (ref 4) and with the NMR study of: Schlabach, M.; Wehrle, B.; Limbach, H.-H.; Bunnenberg, E.; Knierzinger, A.; Shu, A.; Tolf, B.-R.; Djerassi, C. *J. Am. Chem. Soc.* **1986**, *108*, 3856–3858.

(21) The comparison is rather sensitive to the value of the tautomer equilibrium assumed, and this difference quickly diminishes as K is increased toward unity.

S_1 Torsional Potentials of Substituted Anthracenes

David W. Werst, Ann M. Brearley, W. Ronald Gentry,* and Paul F. Barbara*†

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455.

Received June 12, 1985

Abstract: The vibrational structures of jet-cooled 2-phenylanthracene, 9-vinylanthracene, and 9-(2-naphthyl)anthracene have been investigated by laser-induced fluorescence in the frequency range 29900–27600 cm^{-1}. For each molecule the excitation spectrum contains a progression that can be assigned to an excited-state mode corresponding primarily to torsional motion about the bond joining the anthracene ring to the substituent. The experimentally observed vibrational spacings for this mode are modeled well by a simple one-dimensional effective potential in the torsional angle ϕ, of the form $V(\phi) = {}^1/_2\sum_n V_n(1 - \cos n\phi)$. The best-fit potential parameters for the molecule are the following: 2-phenylanthracene, $V_2 = 864$ cm^{-1} and $V_4 = -77$ cm^{-1}; 9-vinylanthracene, $V_2 = 1909$ cm^{-1} and $V_4 = -106$ cm^{-1}; and 9-(2-naphthyl)anthracene, $V_2 = -1087$ cm^{-1} and $V_4 = -1000$ cm^{-1}. However, a comparison of observed vibronic intensities and isotope shifts in the vibrational spacings with those predicted for pure torsional motion shows that the simple one-dimensional-model potential is not completely adequate.

Torsional motion about single bonds is important in many aspects of the study of chemical structure and dynamics. Torsional potential functions have been studied extensively because they are the dominant factor in determining conformational structure, and because they reflect the operation of chemical forces such as conjugation and repulsive nonbonding interactions. Torsional vibrations typically have very low frequencies. Consequently, they make large contributions to the molecular density of states and free energy. In chemical kinetics, torsional motion is important because it is often a major component of the reaction coordinates of organic chemical reactions, especially isomerization.[1-5]

[†] Fellow of the Alfred P. Sloan Foundation, 1984–1985, and Presidential Young Investigator, 1984–1989.

(1) (a) Syage, J. A.; Felker, P. M.; Zewail, A. H. *J. Chem. Phys.* **1984**, *81*, 4685. (b) Syage, J. A.; Felker, P. M.; Zewail, A. H. *J. Chem. Phys.* **1984**, *81*, 4706.

(2) (a) Velsko, S. P.; Fleming, G. R. *J. Chem. Phys.* **1982**, *76*, 3553. (b) Loufty, R. O.; Arnold, B. A. *J. Phys. Chem.* **1982**, *86*, 4205. (c) Courtney, S. H.; Fleming, G. R.; Khundkar, L. R.; Zewail, A. H. *J. Chem. Phys.* **1984**, *80*, 4559. (d) Keery, K. M.; Fleming, G. R. *Chem. Phys. Lett.* **1982**, *93*, 322. (e) Shepanski, J. F.; Keelan, B. W.; Zewail, A. H. *Chem. Phys. Lett.* **1983**, *103*, 9.

0002-7863/87/1509-0032$01.50/0