primarily depend on the cation size. For example, the reduced crown **4** is free to wrap around the small Mg^{2+} cation (r = 0.66 Å) in the same manner as for the Li^+ (r = 0.68 Å) complex. The two coordinated (ion-paired) nitrate anions prevent such a conformational change in the $Mg(NO_3)_2$ complexes of the aliphatic crowns,[7] which illustrates the significant influence ion pairing can have on the structure of the macrocycle–cation complex.

NMR Spectra of Complexes of 2 and 4. Although the CD spectrum of **2** is unaffected by addition of metal cations, the ^1H NMR spectrum of this crown indicates that the methylene portion of the ring undergoes conformational changes upon complexation. There are two distinct groups of methylene protons which exhibit overlapping resonances in the spectra of both free and complexed **2**. The methylene protons α to the methyl substituents constitute one group and form an ABX spin system with the chiral proton H_x. The ether units (OCH_2CH_2O) comprise the second group and form a four-spin AA'BB' coupled system. Because of extreme overlap between the AA'BB' and ABX methylene resonances even at 300 MHz, these spectra could not be analyzed by using the pertinent relationships[36] nor could they be fit in a unique manner by using the iterative program PANIC.[37] Nevertheless, although a complete analysis of the methylene resonances is not possible with use of these spectra alone, the following qualitative observations can be made. The AA' portion of the spectrum is partially resolved in the spectrum of uncomplexed **2** and appears to be the typical pattern observed when the methylene units are undergoing rapid interconversion between the syn- and anti-gauche rotamers.[34] In the presence of a cation this pattern collapses and broadens, suggesting that rotamer interconversion is slower.

The overlap of the AA'BB' and ABX patterns is even more severe in the case of **4** (Figure 8). However, the peak(s) due to the methylene protons α to the pyridine ring are clearly resolved. These protons form an AB spin system since they are magnetically inequivalent. Despite being inequivalent, they appear as a singlet in uncomplexed **4**, meaning that the chemical shifts of H_a and H_b are nearly equal. This observation is consistent with rapid rotamer interconversion, which would average the chemical shifts. Complexed **4** exhibits an AB doublet pattern (Li^+, J = 15.3 Hz, $\delta\nu$ = 29.1 Hz; Na^+, J = 13.0 Hz, $\delta\nu$ = 35.6 Hz). As noted previously, complexation is known to slow rotamer interconversion, due to the cation–oxygen interaction. These results are also consistent with the observation of CD only for the *complexes* of **4**, particularly since the CD is most sensitive to the conformation of this portion of the crown.

Conclusion

It is clear that the sector rules provide a simple yet adequate framework for the interpretation of induced CD in the near-UV pyridine transitions. The structures these rules predict are reasonable and in accord with the NMR data. This last conclusion may seem unwarranted at first since the NMR spectra of complexes of **2** indicate that the methylene portion of the ring changes with complexation, while the CD of **2** is unaffected by the presence of cations. However, the sector rules predict that the sign and intensity of the CD for **2** in the coplanar conformation are determined by the positions of the methyl groups. Since these are located on the rigid portion of the macrocyclic ring, their positions, and thus the CD, are insensitive to complexation. In contrast, the chiral centers of both **3** and **4** are located on the more flexible methylene portion of the ring and consequently the CD is much more sensitive to conformational changes due to complexation than for **1** and **2**. Thus, both the CD and NMR data are consistent with the increased rigidity of these crowns in the presence of a central cation.

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NMR Spectra of Porphyrins. 31.[1] Ring Currents in Hydroporphyrins

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Abstract: The dipole–dipole network model of the porphyrin macrocyclic ring current is used to investigate the ring currents in reduced (hydro)porphyrins derived from phylloerythrin methyl ester. Reduction of ring D to afford the corresponding chlorin results in a decrease of the inner loop and pyrrole subunit ring currents by about 10%. Further reduction of another pyrrole ring gives very different results depending upon the pyrrole ring reduced. In bacteriochlorophyll *a*, in which the opposite pyrrole subunits (B and D) are reduced, there is a further 10% reduction in the pyrrole ring current and a 20% reduction of the inner loop ring current. In the isobacteriochlorin system (rings A and D reduced) there is a much larger decrease in the inner loop ring current, to about 45% of the chlorin value. In the pyrrocorphin (hexahydroporphyrin) system (rings A, B, and D reduced) there is a further 10% decrease in the pyrrole ring current and the inner loop ring current is only 25% of the chlorin value. These results are discussed in terms of steric effects in the macrocycle. The ring current models thus obtained are used to investigate structural and conformational differences in the various isobacteriochlorin isomers.

Recently, there has been an upsurge of interest in the highly reduced porphyrin systems,[4a] catalyzed by the discovery of the isobacteriochlorin prosthetic group in the nitrite and sulfite reductases[4b] and heme d_1[4c] and the structure of the nickel containing

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factor F430 from methanogenic bacteria.[4d] To this end, the syntheses of nickel(II) isobacteriochlorins and pyrrocorphin models have been described,[5] together with a detailed analysis of the proton NMR spectra. However, there has been, to date, no investigation of the extent to which the aromatic ring current of the porphyrin ring, which dominates the chemical shifts of the porphyrin protons, is preserved or modified in these hydroporphyrin systems.

In previous parts of this series[6-8] we have described a ring current model of the porphyrin ring which has been precisely calibrated and then applied successfully to investigate a variety of phenomena involving the porphyrin anisotropy. These include studies of ligand conformation and geometries in metalloporphyrins[7-9] and also aggregation phenomena of various kinds in both free base and metalloporphyrins.[10] The ring current model was subsequently adapted to the reduced porphyrin ring system of chlorophyll,[11] and it was shown that both the introduction of the C-9 keto function and the reduction of ring D had an effect on the inner loop ring current, giving a decrease of about 6 and 10%, respectively, of the porphyrin ring current. This model of the chlorophyll ring system was then applied to the complex problems of aggregation in both chlorophyll (Chl) and bacteriochlorophyll *d* (BChl-*d*),[12] resulting in the proposal of novel aggregate structures.

Here we wish to investigate both the applicability of the ring current model to highly reduced porphyrin systems and also to obtain, via the model, a quantitative estimate of the aromatic ring current in these hydroporphyrin systems. As we shall show, the ring current is a very sensitive measure of the degree of conjugation or strain in these reduced rings and is not solely a function of the number of available π electrons. Also, a well-parametrized ring current model may be used both intramolecularly (e.g., to confirm assignments in the proton NMR spectrum and to probe conformational changes in the macrocycle) and intermolecularly in aggregation phenomena. An example of the former application is given here.

Theory

There are a number of models of the porphyrin ring current[13,14] based on the Johnson–Bovey current loop calculation,[15a] the Haigh–Mallion quantum mechanical approach,[15b] or the equivalent dipole model.[15c] As was emphasized and illustrated some time ago (Figure 2 in ref 16), the equivalent dipole and current loop models are identical at sufficient distances from the current loop. The network model,[6,7] in which the porphyrin ring current is broken down into eight double dipoles, has the advantage of reducing this critical distance to about 3.6 Å, and at smaller distances than this, a close range facility is incorporated into the model (see later).

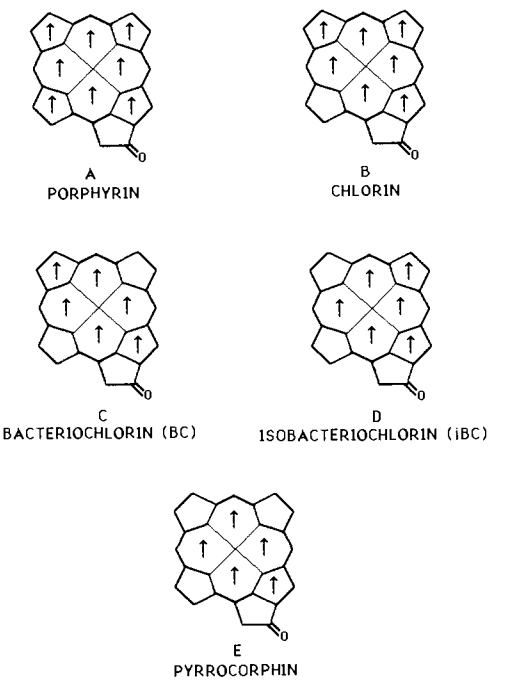

Figure 1. The dipole network for the porphyrin (A), chlorin (B), bacteriochlorin (C), isobacteriochlorin (D), and pyrrocorphin (E) rings derived from phylloerythrin methyl ester (**1a**).

The double dipole model for the porphyrin ring current has been described in detail,[6,7,9] so only a brief summary is presented here. The ring current loops in the porphyrin macrocycle are replaced by their equivalent dipoles, and the total ring current shift at any point (R) is obtained as the sum of the contributions of the equivalent dipoles by using the standard dipole–dipole equation. This gives the basic equation

$$\delta_R = \mu_H \sum_{i=1,8} f(iR) + \mu_P \sum_{i=1,8} f(jR) \qquad (1)$$

where $f(iR) = [1 - 3(Z_R \pm 0.64)^2/r_{iR}^2]/r_{iR}^3$.

The symmetry of the porphyrin ring allows for only two types of equivalent dipoles, those for the pyrrole rings (μ_P) and those for the hexagons (μ_H). The lower symmetry of the chlorin ring provides for two different types of pyrrole ring (i.e., rings A and C, and ring B) and two types of hexagon (Figure 1). Thus, there are four different values of the equivalent dipoles. In the bacteriochlorin (BC) and isobacteriochlorin (iBC) rings there is more symmetry (excluding the C-9 keto function) than in the chlorin; thus there would appear to be no reason to consider any variation of the ring currents within the pyrrole rings. We therefore retain eq 1 as our fundamental equation, with the incorporation of the "close range approximation".[11] In this, the ring current shift of any nucleus, of coordinates x, y, z, close to the porphyrin ring (defined by a cylinder of height d and radius r), is given by

$$\delta = \delta_d + g_d[b(d^2 - z^2) + c(d^4 - z^4)] \qquad (2)$$

where $c = -(1 + 2bd)/4d^3$. δ_d and g_d are the calculated shift and gradient at the close range boundary (x, y, d), and b is an arbitrary parameter. The values of b and d obtained previously[11] of −0.64 and 3.6 Å will be used henceforth.

In order to obtain a ring current model for the reduced porphyrin rings the ring current shifts of a number of protons in molecules of known geometry must be obtained. We shall adopt here the procedure used previously with success for the chlorin ring system[11] of referring the proton chemical shifts in the reduced rings to those of the analogous less-reduced compound, i.e., we compare calculated and observed shift differences for chemically similar protons. For this approach to hold the substituent shifts at the protons must be identical in the two systems; thus the molecules should have identical substituents but differ only in the

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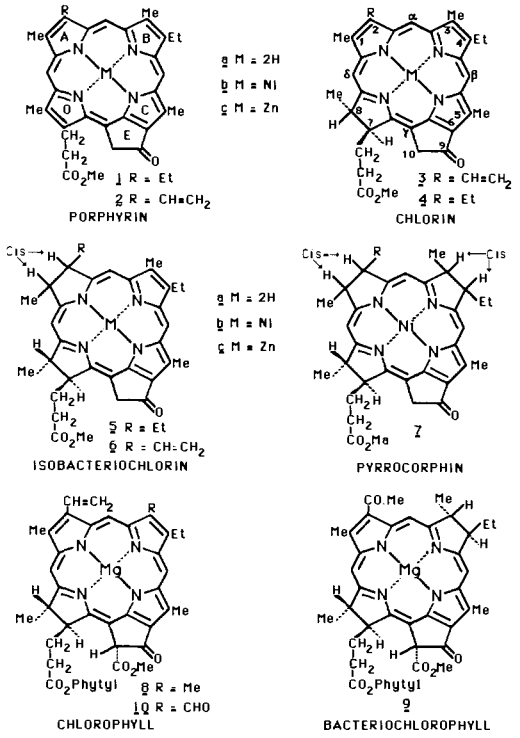
Chart I



presence of the reduced rings. Further criteria are the requirements in all compounds of accurately measured and well assigned spectra with no aggregation shifts. A series of molecules fulfilling all of these criteria is the reduced porphyrins derived from phylloerythrin methyl ester (**1a**) and its 2-vinyl analogue **2a**. The free base and zinc(II) porphyrins together with the corresponding chlorins [methyl pyropheophorbide *a* (**3a**) complexes] were used in our previous studies of the chlorin ring current.[11] Thus, it was both appropriate and expedient to consider the nickel(II) (**5**, **7**)[5a] and zinc(II) (**6**)[5b] hydroporphyrin analogues of these systems which have recently been synthesized.[5] We include also some literature data on BChl-*a*[17] (**9**) for which a direct comparison with Chl-*a*[18] (**8**) is appropriate for all but a few protons.

We had originally intended to use the appropriate nickel(II) porphyrins as direct analogues of the reduced nickel(II) derivatives. However, dilution studies of nickel(II) 2-vinylphylloerythrin methyl ester (**2b**) showed pronounced concentration effects due to aggregation, even down to very low concentrations ($<10^{-3}$ M). Furthermore, the aggregates were not broken down by the addition of small amounts of pyridine or methanol, in contrast to the corresponding zinc(II) compounds **2c**. The addition of stronger bases such as piperidine causes the nickel(II) to become paramagnetic.[19] Thus, the nickel(II) porphyrins cannot be used to obtain precise chemical shift data without, for example, extrapolation to infinite dilution, a tedious procedure. Fortunately, the nickel(II) hydroporphyrins showed no evidence of these aggregation effects, the chemical shifts being essentially independent of concentration. The corresponding zinc(II) compounds do show aggregation effects, but these are always destroyed by addition of small amounts of pyrrolidine or pyridine to yield concentration independent shifts.

The geometry of the chlorin ring was taken from the X-ray studies of ethyl chlorophyllide *a* dihydrate[20] and of methyl pheophorbide *a*.[21] In these molecules the ring skeleton is essentially flat and unchanged by the addition of a magnesium atom in the former. There is no evidence that introduction of a zinc(II) atom causes any significant perturbation of the chlorin or porphyrin rings, which may be considered identical apart from ring D. In these molecules ring D has almost C_2 symmetry, with C_7 out of the plane of the other ring atoms. Introduction of nickel(II) can cause significant distortions in the macrocycle geometry. In nickel(II) octaethyl-iBC the pyrroline rings are shallow half-chairs having C_s symmetry with diequatorial ethyl substituents.[22] The conformations of these rings can thus vary from half-chair (C_s) symmetry to C_2 symmetry with consequent changes in the positions of the substituents, which may be pseudoaxial or pseudoequatorial. We shall show that this can significantly affect the chemical shifts of the substituents. The X-ray structure[23] of nickel(II) iBC **5b** (tcc isomer)[5a] showed a ruffled macrocycle with rings A and D in half-chair conformations. Here we will assume that the basic macrocycle is not seriously deformed from the planar geometry, while noting the above caveat concerning the geometries of the reduced rings. In any case, when a pyrrole subunit is reduced the immediate substituents cannot be used to check any ring current variations as the chemical environment of the substituents will have changed appreciably. For example, on reduction of ring D the C_8-Me is attached to a saturated carbon atom instead of an unsaturated one in the porphyrin, and thus the difference in the chemical shifts of the methyl (on going from porphyrin to chlorin) is not only due to changes in the ring current. However, further reduction of rings A and B does not affect the chemical environment of the C_8-Me and therefore this chemical shift difference can be used for investigation of the bacteriochlorin ring currents.

Table I. Proton Chemical Shifts (δ, ppm) of 2-Vinylphylloerythrin Methyl Ester (**2a**) and the Analogous Hydroporphyrins

proton		**2a** Zn complex + pyrr[a] (**2c**)	methyl pyropheophorbide *a* Zn complex + pyr[a] (**3c**)	methyl pyropheophorbide *a* Ni complex (**3b**)	iBC Zn complex + pyr (**6c**)
meso	β	9.925	9.521	9.296	8.323
	α	9.811	9.258	9.076	7.019
	δ	9.685	8.316	8.160	6.463
vinyl	CH	8.237	8.013	7.760	6.08
	Ht	6.346	6.160	6.021	5.36
	Hc	6.142	5.996	5.965	5.27
C_{10}-H_2		5.810	5.145	4.840	4.42
			5.019	4.800	4.28
C_4-CH_2		3.961	3.714	3.600	3.20
CO_2-Me		3.778	3.533	3.595	3.54
β-Me	C_5	3.880	3.655	3.475	3.11
	C_1	3.644	3.302	3.153	1.46
	C_3	3.486	3.215	3.124	2.60
	C_8	3.486	1.682	1.535	1.38
C_4-Me		1.827	1.672	1.604	1.39
CH_2-CH_2		4.128	2.54	2.43	2.23 (2)
		3.048	2.45	2.25 (2)	2.08
			2.24	2.12	2.00
			1.92		
C_7-H			4.17	3.990	3.43
C_8-H			4.36	4.277	3.70
C_1-H					4.00
C_2-H					4.51

[a] pyrr = pyrrolidine, pyr = pyridine-d_5.

Results and Discussion

Tables I–III record the proton chemical shifts of the compounds considered here. For convenience the results for zinc(II) 2-vinylphylloerythrin methyl ester (**2c**) and zinc(II) methyl pyropheophorbide *a* (**3c**), from ref 11, are included along with those for the nickel(II) methyl mesopyropheophorbide *a* (**4b**), iBC **5b**,

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Table II. Proton Chemical Shifts (δ, ppm) of Phylloerythrin Methyl Ester (**1a**) and the Analogous Hydroporphyrins

proton		**1a** Zn complex + pyr[a] (**1c**)	methyl mesopyropheophorbide *a* Zn complex + pyr (**4c**)	methyl mesopyropheophorbide *a* Ni complex (**4b**)	Ni-iBC band 1 (**5b**) (ttc)	Ni-iBC band 2 (**5b**) (tcc)	Ni-Pyrrocorphin (**7**)
meso	β	9.939	9.48	9.26	8.185	8.203	6.63
	α	9.652	9.05	8.99	7.086	7.033	6.18
	δ	9.648	8.21	8.08	6.399	6.506	5.99
C_{10}-H_2		5.829	5.12	4.85	4.220	4.203	3.91
			4.99	4.75	4.172	4.173	3.77
C_2-CH_2		3.932	3.70	3.53	1.76	2.26	1.64
					1.35	2.01	1.10
C_4-CH_2		3.932	3.70	3.54	3.157	3.163	1.78
					3.127	3.133	
CO_2-Me		3.713	3.53	3.60	3.641	3.637	3.65
β-Me	C_5	3.852	3.64	3.46	2.986	2.992	2.59
	C_3	3.476	3.21	3.02	2.589	2.594	1.04
	C_1	3.476	3.17	3.12	1.615	1.088	1.46
	C_8	3.451	1.67	1.53	1.273	1.278	1.20
C_2-Me		1.789	1.66	1.60	0.817	1.261	0.79
C_4-Me		1.774	1.66	1.60	1.384	1.395	1.15
CH_2-CH_2		4.146	2.50	2.43	2.356	2.339	1.65
		3.031	2.33	2.26 (2)	1.973	1.960	1.8 (2)
			2.23	2.14	1.962		2.10
			1.90				
C_7-H			4.11	3.96	3.280	3.284	2.91
C_8-H			4.30	4.25	3.520	3.503	3.19
C_1-H					3.878	3.762	3.54
C_2-H					3.479	3.570	3.16

[a] pyr = pyridine-d_5.

Table III. Observed Chemical Shifts (δ, ppm) and Observed and Calculated Shift Differences ($\Delta\delta$, ppm) of Equivalent Protons in Chlorophyll *a* (**8**) and Baceteriochlorophyll *a* (**9**)

proton		chlorophyll *a*[a] (**8**)	bacterio-chlorophyll *a*[b] (**9**)	shift differences obsd	shift differences calcd[d]
meso	α	9.39 (9.87)[c]	8.81	0.58 (1.06)	1.12
	β	9.71	8.43	1.28	1.12
	δ	8.55	8.38	0.17	0.42
C_{10}-H		6.19	5.90	0.29	0.26
		4.173	3.77		
C_5-Me		3.60	3.30	0.30	0.31
C_7-H		4.18	4.00	0.18	0.18
C_8-H		4.56	4.40	0.16	0.17
C_8-Me		1.77	1.67	0.10	0.15
C_3-Me		3.29	1.76	(1.53)	0.82

[a] 1.6 mM in acetone-d_6 (ref 18). [b] In acetone-d_6 (ref 17). [c] In chlorophyllide *b* (ref 25), 0.1 M in $CDCl_3$ plus methanol-d_4. [d] Chlorophyll *a* (**8**) μ_P 14.6, μ_H 16.5; bacteriochlorophyll *a* (**9**) μ_P 13.6, μ_H 13.5.

and pyrrocorphin **7** from ref 5a. The results for Chl-*a* (**8**) and BChl-*a* (**9**), in the same acetone solvent, are from ref 18 and 17.

Of the new compounds reported here, the spectra of the zinc(II) phylloerythrin methyl ester (**1c**) and zinc(II) methyl mesopyropheophorbide *a* (**4c**) are first order at 360 MHz apart from the resonances of the propionate side chain. The assignments were based on those given previously for the corresponding 2-vinyl compounds as only the protons adjacent to the C_2 substituent are significantly affected. The assignments for the nickel(II) methyl pyropheophorbide *a* (**3b**) are also straightforward except for the β-methyl protons; again, these were assigned largely by analogy with the zinc(II) compound, as the shift differences are minor for these protons.

The zinc(II) iBC (**6c**) spectra showed evidence of a mixture of diastereomers, as most of the single peaks were resolved into at most three constituents, in the ratio of about 1:6:1. The assignments given were confirmed by extensive decoupling experiments, and the chemical shifts recorded are for the major diastereomer. The differences between the isomers are very small, except at the site of reduction, i.e., the C_1 and C_2 substituents. This can be seen more clearly in the spectra of the nickel(II) iBCs **5b** in which the isomers could be separated (Table II). Apart from the δ proton and the C_1 and C_2 substituents, the chemical shifts of the protons in these molecules differ by less than 0.05 ppm, and thus we may take the average chemical shift as characteristic of this macrocycle without any appreciable error. The larger chemical shift differences around the reduced ring A can be explained on conformational grounds (see later).

Ring Current Models

(a) Chlorins. The data in Tables I–III can now be used to investigate ring current variations in the hydroporphyrins. We have already shown[11] that incorporation of the C_9 keto group reduces the ring current of the porphyrin ring by about 6%, i.e., the values of the equivalent dipoles are reduced from 17.1 (μ_P) and 19.3 (μ_H) to 16.1 and 18.1, respectively; thus we may take these as base values for the phylloerythrin ring. We have shown, moreover, that reduction of ring D causes an additional decrease in both the pyrrole and inner loop ring currents of about 10%, i.e., the appropriate μ_P and μ_H vallues are 14.6 and 16.5, respectively. The observed shift differences of the corresponding protons in both the 2-vinyl and 2-ethyl (meso) series on going from the phylloerythrin to the analogous chlorin are given in Table IV, together with the calculated shift differences. There is essentially complete agreement, confirming our previous results. The major discrepancies between the observed and calculated shifts can be readily explained on steric and chemical grounds. For example, the larger shift difference observed for the C_{10} CH_2 protons has a simple explanation in terms of the relief of steric interactions with the C_7 side chain upon reduction of ring D, and an analogous explanation may hold for the δ meso proton and the relief of any interactions with the C_8 methyl group. As previously mentioned, the observed change in chemical shift of the C_8 methyl group includes a contribution due to re-hybridization of the neighboring carbon atom (e.g., CH_3 of propene ca. 1.7 ppm vs. propane ca. 0.9 ppm)[24] and is only included for completeness. The conformation of the C_2 and C_4 ethyl groups was considered as orthogonal to the ring plane, and that of the C_2 vinyl group will be considered subsequently. The shift differences calculated for the vinyl protons in going from porphyrin to chlorin are independent of the orientation of the vinyl group, provided that the same orientation is adopted for both systems. The conformation obtained is based on the chlorin/iBC data, which is a function of the vinyl torsional

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Table IV. Observed and Calculated Chemical Shift Differences ($\Delta\delta$, ppm)

		porphyrin to chlorin			chlorin to iBC			iBC to pyrrocorphin	
proton		2-vinyl[a]	2-ethyl[b]	calcd[c]	2-vinyl[d]	2-ethyl[e]	calcd[c]	2-ethyl[f]	calcd[c]
meso	α	0.55	0.60	0.46	2.24	1.93	1.99	0.86	1.09
	β	0.40	0.48	0.46	1.20	1.07	1.35	1.56	1.36
	δ	1.37	1.44	1.15	1.86	1.63	1.95	0.46	0.54
vinyl	CH	0.22		0.21	(1.93)		1.07		
	H*t*	0.19		0.19	0.80		0.93		
	H*c*	0.14		0.11	0.73		0.58		
C_{10}-H_2		0.67	0.71	0.54	0.73	0.58	0.59	0.30	0.35
		0.79	0.84		0.74			0.40	
C_2-CH_2			0.23	0.23					
C_4-CH_2		0.25	0.23	0.20	0.51	0.40	0.50	1.38	0.86
								1.35	0.98
β-Me	C_1	0.34	0.31	0.30	(1.84)		1.11	0.16	
								−0.37	
	C_3	0.27	0.27	0.20	0.62	0.43	0.56	(1.55)	0.87
	C_5	0.22	0.21	0.22	0.54	0.47	0.47	0.40	0.47
	C_8	(1.80)	(1.78)	0.98	0.30	0.25	0.43	0.08	0.17
C_2-Me			0.13	0.12		0.34			
						0.78			
C_4-Me		0.16	0.11	0.10	0.28	0.21	0.27	0.24	0.36
C_7-H					0.74	0.68	0.73	0.37	0.33
C_8-H					0.76	0.74	0.79	0.32	0.31
C_1-H								0.34	0.36
								0.22	
C_2-H								0.32	0.40
								0.41	

[a] Zn vinylphylloerythrin methyl ester (**2c**) → Zn methyl pyropheophorbide *a* (**3c**). [b] Zn phylloerythrin methyl ester (**1c**) → Zn methyl mesopyropheophorbide *a* (**4c**). [c] Porphyrin μ_P 16.1, μ_H 18.1; chlorin μ_P 14.6, μ_H 16.5; iBC μ_P 13.6, μ_H 7.5; pyrrocorphin μ_P 10.0, μ_H 4.0. [d] Zn methyl pyropheophorbide *a* (**3c**) → Zn iBC (**6c**). [e] Ni methyl mesopyropheophorbide *a* (**4b**) → Ni-iBC (**5b**). [f] Ni-iBC (**5b**) → Ni pyrrocorphin (**7**).

angle, and from this the vinyl group points toward the α meso proton with a dihedral angle to the ring of about 40°.

(b) Bacteriochlorin. In this system the model compounds are not as clearly related as the remaining compounds considered here, but the importance of the BC ring system in bacterial photosynthesis in particular warrants its inclusion. Table III gives the observed shift differences between analogous protons of Chl-*a* (**8**) and BChl-*a* (**9**), both at high dilution in the same disaggregating solvent, acetone-d_6, together with those calculated for a small decrease of about 7% in the pyrrole ring current and a larger decrease of 18% in the inner loop ring current. The agreement is precise for those protons situated away from ring A, with the possible exception of the β-proton. The deviation of the observed and calculated shifts for the β-proton almost exactly corresponds to that of the δ-proton in the porphyrin → chlorin series (Table IV) and could well be for the same reason, i.e., relief of the C_4-ethyl interaction in the BC.

However, for those protons adjacent to ring A, in particular the α and δ meso protons, the perturbing influence of the C_2 acetyl group in BChl-*a* (**9**), which is not present in Chl-*a* (**8**), precludes any meaningful comparison of the observed and calculated shifts. Interestingly, the α-proton shift for Chl-*b* (**10**), with a C_3-formyl group, is much closer to the prediced shift, but the α and δ meso proton shifts in 2-acetyl-Chl-*a* would be the correct analogy. Even without these meso proton shifts the system is still over-determined (two unknowns in six equations) and therefore the values of the equivalent dipoles obtained should be reasonably accurate.

(c) Isobacteriochlorins. The chemical shift differences between the chlorin and the analogous iBC may be examined in detail in both the 2-vinyl and 2-ethyl series from the data in Tables I and II, in one case utilizing the appropriate zinc(II) derivatives and in the other the nickel(II) compounds. The differences in chemical shifts for the two series are given in Table IV and show a pleasing consistency, though the shift differences for the nickel(II) compounds are invariably less than those of the corresponding protons in the zinc(II) derivatives. This is clearly due to the difference in chemical shifts of the zinc(II) **4c** and nickel(II) **4b** methyl mesopyropheophorbides *a* (Table II) in which the proton chemical shifts of the nickel(II) compound are always significantly upfield of those of the zinc(II) isomer. This is an intrinsic effect of the nickel atom as the chemical shifts of **4b** were concentration independent.

Comparison of the observed shift differences with those calculated for a small (7%) decrease in the pyrrole ring currents and a pronounced (55%) decrease in the inner loop ring current is given in Table IV. Again, all the protons situated away from the reduced ring A give observed and calculated shift differences in good agreement, with the possible exception of the C_8-Me and the C_{10}-CH_2. This could suggest slightly different conformations of ring D in the chlorin and iBC, but without further data such as a definitive series of crystal studies it is not possible to test this. The α meso proton in the 2-vinyl series is more shifted than calculated, and this is very probably due to the different orientation of the vinyl substituent in the chlorin and iBC. In the iBC the coupling between the vinyl CH proton and the C_2-H is about 8 Hz, which indicates an anti orientation of the protons; thus the vinyl group is cis to C_2-H. In the chlorin (and porphyrin) the orientation of the vinyl group has been open to question. In the crystal of methyl pheophorbide *a* the vinyl Cβ atom is 0.23 Å out of the macrocyclic ring plane pointing toward the C_1 methyl,[21] whereas in the crystal of ethyl chlorophyllide *a* the vinyl Cβ atom is 0.5 Å out of the ring plane pointing toward the Cα meso proton.[20] Our data are more in accord with the latter results, though crystal packing interactions are such that there is no good reason for the orientation of the vinyl group to be the same in solid and solution. Thus the orientation of the vinyl group was varied in the chlorin, keeping the vinyl group pointing toward the Cα meso proton. The calculated shift differences in Table IV are for a torsional angle of 40° corresponding to a displacement of the Cβ carbon atom of 0.64 Å from the ring plane. The observed and calculated shift differences for H*t* and H*c* are in reasonable agreement (the observed shift of the =CH proton includes a hybridization factor from the C_2 carbon), providing support for this conformation. The differing conformations of the C_1 and C_2 substituent groups in the nickel iBCs will be considered subsequently.

(d) Pyrrocorphin (hexahydroporphyrin). In the pyrrocorphin series the sole method of preparation of this compound [Raney nickel reduction of the nickel(II) chlorin][5a] necessitated the presence both of the nickel(II) atom and a 2-ethyl in the product **7**. However, there is a precise analogy with the corresponding nickel(II) iBCs, and the shift differences for corresponding protons are given in Table IV, together with the calculated values for a further 26% reduction in the pyrrole ring currents and a larger

(47%) reduction in the inner loop ring current compared with the iBC.

The agreement is very good for those protons of corresponding conformations in the two compounds. The major discrepancies are very probably due to conformational differences in the macrocycle in the two series, as there would be a much smaller tendency toward planarity in the macrocycle of the pyrrocorphin, with three reduced pyrrole rings, than in the other molecules. With this caveat, the meso proton shifts are in good agreement with the calculated values (note again the consistent excess of about 0.20 ppm in the meso proton between two pyrrole rings on reducing one of them, in this case the β-proton). The calculated shift differences for the other ring protons (C_{10} CH_2, C_7 H, C_8 H) and the only remaining β-methyl attached to a pyrrole ring (Me-5) are in excellent agreement with the observed shift differences. Note also the very consistent hybridization shift of a β-methyl group upon reduction of the attached pyrrole ring (0.82, 0.73, 0.68 ppm). The shift differences of the substituents on ring A in the iBC **5b** are very dependent on the conformation of ring A and on the orientation of the substituents (see later). However, the shifts of the C_1H and C_2H protons are not so dependent, and the shift differences are included in Table IV. There is again good agreement with the shift differences calculated on the basis of a similar ring A conformation in the iBC and the pyrrocorphin.

Conformational Effects

With the parametrization of the ring current models attained, it is of interest to see whether these models can be used to explain the quite large differences observed in the substituent chemical shifts of the C_1 and C_2 substituents in the iBC. For example, the C_1 methyl in the two isomers studied occurs at 1.61 and 1.09 ppm, a very considerable difference which is certainly not due to any anisotropic effects of the neighboring substituents. Fortunately in this series the crystal structure of the band 2 isomer (**5b**, tcc isomer) has been obtained,[23] and also extensive decoupling data[5a] provide further information about the side chain conformations in solution. Thus a reasonable geometric model can be constructed as follows. The conformation of ring A is a half-chair with C_1 down and C_2 up from the ring plane, so that in this isomer (tcc from ring D) the C_1 and C_2 substituents are pseudoaxial and pseudoequatorial, respectively. In the crystal the conformation of the C_2 ethyl group is gauche with respect to H_2 and the observed coupling constants between H_2 and the H_{2a} protons (3.9 and 10.6 Hz)[5a] indicate that this conformation is strongly favored in solution. On this basis, the calculated ring current shifts for the C_1 methyl and the C_2 methylene and methyl protons are 0.064 (Me), 0.53, 0.68 (CH_2CH_3), and 0.27 (CH_2CH_3).

The crystal structure of the band 1 isomer (**5b**, ttc isomer) has not been determined, but assumption of a similar conformation with cis addition to ring A gives the C_1 and C_2 substituents a pseudoequatorial and pseudoaxial conformation. Furthermore, the C_2H, $C_{2a}H_2$ couplings (4.6, 4.0 Hz) can only mean a predominant conformation of the C_2 ethyl group in which the C_2-CH_3 is anti to H_2. On the basis of this conformation the ring current shifts of the C_1-Me and C_2 ethyl protons are calculated as 0.44, 0.12, and 0.27 (CH_2CH_3) and −0.45 (CH_2CH_3) ppm. The observed and calculated (in parentheses) shift differences (band 1 isomer − band 2 isomer) for these protons are thus C_1-Me 0.53 (0.38), C_2-CH_2 −0.50, −0.66 (−0.41, −0.41), and C_2-Me −0.44 (−0.72).

The observed shift differences are reasonably well reproduced considering the necessary assumptions made over the precise geometry of the molecules. It would appear that, given a reasonably accurate molecular geometry, the ring current model is capable of predicting shifts (or rather shift differences) to within the experimental accuracies, and thus could be of considerable assistance in conformational and even structural problems involved in hydroporphyrin systems.

Conclusions

Our analysis of the observed proton chemical shifts of the reduced zinc(II) and nickel(II) phylloerythrin methyl ester derivatives shows that the double–dipole network model of the porphyrin ring current may be applied, when suitably parametrized, to give reasonably accurate predictions of the effects of the reductions of successive pyrrole subunits on the substituent proton chemical shifts.

The values of the ring currents obtained for the reduced systems are of considerable interest. Taking the values of the equivalent dipoles of phylloerythrin methyl ester as the base (100%), the inner loop and pyrrole ring currents in the series chlorin, BC, iBC, and pyrrocorphin are 91 and 91%, 75 and 84%, 41 and 84%, and 22 and 62%, respectively. The two aspects of major interest in this series are the considerable difference in the inner loop ring current of the BC and iBC rings and the tendency of the pyrrole ring current to be maintained even when the inner loop ring current is reduced to a small proportion of the original porphyrin ring current value.

The much greater inner loop ring current in the free base BC compared with the analogous iBC would have an obvious rationale in terms of steric effects of the NH protons. In the reduced porphyrin macrocycle there is a general pronounced tendency for the NH protons to avoid the reduced pyrroline ring; thus, in the free base chlorin the NH protons are invariably situated on rings A and C, in the favored "opposite" orientation. In the BC, this orientation is still possible, but in the iBC there is now competition between this favored opposite orientation of the NHs and the tendency to be attached to the nonreduced pyrrole rings. This would tend to destabilize the macrocycle in an exactly analogous manner to the effects of protonation in the porphyrin ring, resulting therefore in a reduced ring current. What is of interest is that this behavior is present in the zinc(II) and nickel(II) complexes in which steric effects due to NH protons are absent. Thus it would appear that the reduction of the inner loop ring current in the iBC ring system is an intrinsic property of this reduced ring. This could be due to a more buckled conformation of the macrocycle in the iBC than in the BC system (in which the reduced rings are well separated, favoring coplanarity).

The tendency of the pyrrole rings to maintain their aromatic character was recognized some time ago by Woodward,[26] and our results further support this concept. The intriguing question of the possible presence of an aromatic ring current in those hydroporphyrin systems in which the macrocyclic conjugation has been broken (e.g., by reduction at the meso positions)[27] will be considered in a future paper.[28]

Experimental Section

Proton NMR spectra were measured at 360 MHz on a Nicolet NT-360 spectrometer. Chemical shifts (δ) are reported relative to $CHCl_3$ at 7.260 ppm. Typical conditions were the following: probe temperature 23 °C, 16 or 32 K data points, sweep width 4 kHz giving a digitization accuracy of 0.25 or 0.5 Hz/point, pulse width 7 μs, acquistion time 1 or 2 s, and ca. 80 accumulations.

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