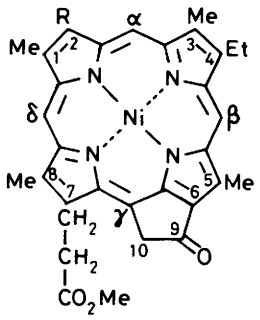
Nuclear Magnetic Resonance Spectra of Porphyrins. Part 33.[1] Ring Currents in Nickel(II) Hydroporphyrins Derived from Anhydromesorhodoporphyrin XV

Raymond J. Abraham * and Craig J. Medforth
School of Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX
Kathryn E. Mansfield, Daniel J. Simpson, and Kevin M. Smith *
Department of Chemistry, University of California, Davis, CA 95616, U.S.A.

The double dipole network model of the porphyrin macrocyclic ring current is used to investigate the ring currents in reduced (hydro)porphyrins derived from nickel(II) anhydromesorhodoporphyrin XV methyl ester (**2**). The reduction of ring D to the corresponding chlorin (**3**) results in a decrease of about 10% of the pyrrole ring current, and about 40% in the inner loop current. The marked effect of the nickel(II) atom on the inner loop ring current in the chlorin series is clearly identified; the inner loop ring current is about two-thirds of that previously found for the magnesium(II) and zinc(II) chlorins. Further reduction of rings A and C gives the corresponding isobacteriochlorin isomers [(**4**) and (**5**)], which show an additional decrease of the ring current, this result paralleling that found previously for the nickel(II) isobacteriochlorin from phylloerythrin. The proton chemical shifts in nickel(II) hexahydro- (**6**) and (**7**) and octahydro-porphyrins (**8**), in which one or two of the meso methine carbons have been reduced (and therefore interrupt the inner loop pathway), are best accounted for by the inclusion of a small inner loop ring current in one quadrant of the macrocycle (*i.e. via* the nickel atom), together with ring currents in the unreduced pyrrole rings.

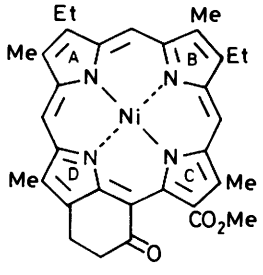
The proton n.m.r. spectrum of a porphyrin or metalloporphyrin is dominated by the large 'aromatic' ring current of the circulating π-electrons of the porphyrin macrocycle,[2] and in previous parts of this series[3] the development of a quantitative model to describe the effects of the ring current on the nuclear chemical shifts of the adjacent nuclei has been formulated, based on a double dipole network model. This model was originally calibrated for the porphyrin ring and used successfully to investigate complexation and aggregation phenomena involving porphyrins and metalloporphyrins.[4] Recently, a more refined model for cobalt(III) tetraphenylmesoporphyrin has been used to determine the conformations of axial ligands complexed to the metal ion.[1,4c,*]

The network model was subsequently parameterised for the chlorin (7,8-dihydroporphyrin) nucleus of chlorophyll,[5] and here both the perturbing effects of the C-9 keto function and of the reduced ring D were incorporated. The complex aggregation behaviour of chlorophylls *a* and *b*, and bacteriochlorophyllide *d*, were analysed on the basis of this ring current model.[4b,6] Very recently, the same procedure was used to investigate ring currents in more reduced porphyrins.[7] This investigation showed how the inner loop ring current depended not only upon the number of reduced pyrrole units, but also on their relative position, and also how the ring currents of the non-reduced pyrrole rings tended to maintain their original values. For example, in bacteriochlorophyll *a*, in which the opposite pyrrole subunits B and D are reduced, there is a 10% reduction in the pyrrole ring current and a 20% reduction in the inner loop current compared with the corresponding chlorin. In the isobacteriochlorin system, in which the adjacent pyrrole subunits A and D are reduced, the inner loop ring current drops to 45% of the chlorin value but the pyrrole ring currents are the



(1)

R = Et or vinyl



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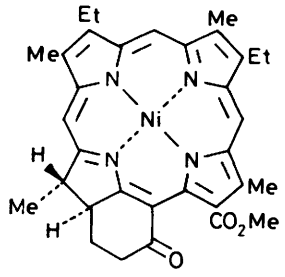

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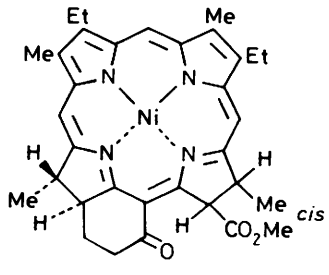

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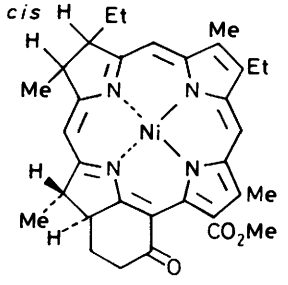
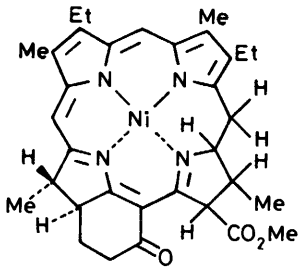


(5)

† *Editor's note.* Throughout the text, the Fischer form of nomenclature and numbering has been used; this differs from that recommended by the IUPAC authorities for such compounds. As an example of the differences which arise application of the IUPAC rules of nomenclature to compound (**3**) would lead to the following name: (8,13-diethyl-2,2^1,2^2,2^3-tetrahydro-18-methoxycarbonyl-3,7,12,17-tetramethyl-2^3-oxo-3*H*-benzo[*at*]porphyrinato)nickel(II).



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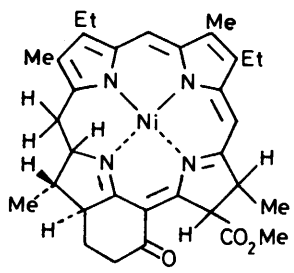

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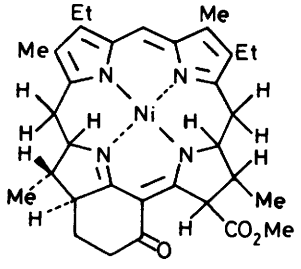


(8)

same as in bacteriochlorophyll *a*. In the analogous pyrrocorphin (hexahydroporphyrin) system the inner loop ring current is only 25% of the chlorin value. In all these investigations the reduced porphyrins were all derived from phylloerythrin methyl ester, but synthetic considerations precluded the use of a completely homologous series of compounds. Thus, it is of some interest to determine the generality or otherwise of these novel findings and to see whether they are an intrinsic function of the macrocycle or in any way influenced by the substituents or the central metal ion.

Recent synthetic advances[8] have allowed the synthesis of a series of nickel(II) hydroporphyrins all bearing the same anhydrorhodoporphyrin skeleton. Furthermore, this series of products also comprise the corresponding hexahydro- and octahydro-porphyrins which are reduced at one or two meso positions, thereby destroying the conjugation pathway for the inner loop ring current. It is of some interest to determine, using the double dipole model, whether in these compounds the central metal atom could be utilised to provide a pathway for the circulating π-electrons, *i.e.* whether the introduction of the metal would enhance the aromaticity of the system.

We address these questions here and show that the results obtained in the phylloerythrin series (**1**) are corroborated in the anhydrorhodoporphyrin (**2**) cases, and also that the central nickel atom in the 'deconjugated' hexa- and octa-hydroporphyrins studied does show a small tendency to provide a pathway for the circulating π-electrons. This may well be related to the phenomenon of co-ordinate hole contraction which occurs in hydroporphyrins complexed to low-spin nickel(II).[9]

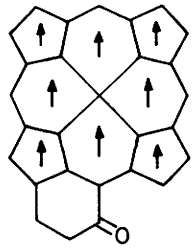
Theory

The double dipole model for the porphyrin ring current has been described in detail,[3,4] so only a brief summary is given 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 using the standard dipole-dipole equation. This gives the basic equation:

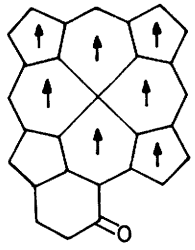
$$\delta_R = \mu_H \Sigma f(iR) + \mu_P \Sigma f(iR) \qquad (1)$$

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

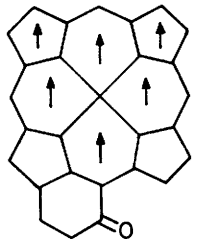
The symmetry of the porphyrin ring allows for only two types of equivalent dipoles, those for the pyrrole rings (μ_P) and for the hexagons (μ_H) assuming that the perturbing effects of the C-10 keto group and the nickel(II) co-ordination unsaturation would not be specific to one region. The lower symmetry 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. Thus, there are four different values, in principle, of the equivalent dipoles. In the isobacteriochlorin ring systems there is more symmetry than in the chlorin whilst the hexahydro ring systems have no symmetry elements. In all previous studies there has not been any necessity to consider any variation of the ring currents within the pyrrole rings of each molecule; thus we retain this approximation here.



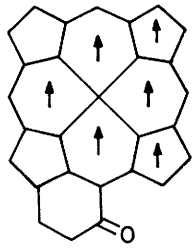
(2)
Porphyrin



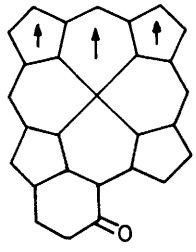
(3)
Chlorin



(4)
Isobacteriochlorin



(5)
Isobacteriochlorin



Hexa - (6),(7) or octa - (8) hydroporphyrins

However, there is no reason to believe that the nickel atom is necessarily centred in the porphyrin hole, as the nitrogen atoms in the hydroporphyrins are no longer equivalent due to both differences in basicity and due to the different flexibility of the various parts of the macrocycle.[9] This aspect is most easily accommodated in the double dipole model by allowing the values of μ_H to vary; thus in the chlorin there will be (in principle) two values of μ_H and in the isobacteriochlorins three values. In the hexahydroporphyrins, although in principle there are three different values of μ_H (one of them being zero), as we shall see the only significant (non-zero) value is that between the unreduced pyrrole rings A and B. This is also the case for the octahydroporphyrin. Thus, we shall retain equation (1) as our

fundamental equation, with the incorporation of the possibility of varying μ_H within the different 'hexagon' rings The 'close range approximation,' as previously defined,[5] remains unaltered. However, as all the shifts investigated here arise from protons at the edge of the macrocycle which are outside the close range area, this approximation does not influence the present calculations.

As previously,[5,7] we compare the ring current shifts of protons in the hydroporphyrins with those of similarly constituted protons in the less reduced compound, *i.e.* we compare calculated and observed shift differences for chemically similar protons. A number of criteria must be satisfied for this procedure to be valid: the substituent shifts at the proton concerned must be identical in the two systems, and thus the molecules should have identical substituents; secondly, the molecular geometry should be known, and in particular the position of the proton considered with respect to the macrocyclic ring current should be accurately known. Furthermore, the spectra should be accurately measured and unequivocally assigned, with no evidence of aggregation shifts.

The preparation and n.m.r. spectra of the series of hydroporphyrins (**2**)—(**8**) have been given previously,[8] except that these compounds were all derived from Raney nickel reduction of the nickel(II) anhydrochlorin (**3**). The preparation of the analogous nickel(II) anhydroporphyrin (**2**) is given in the Experimental section. Surprisingly, the n.m.r. spectrum of the nickel(II) anhydroporphyrin (**2**) showed no evidence of any aggregation effects. On dilution from 7 mM in $CDCl_3$ solution to 0.7 mM there was a slight, non-specific increase in the chemical shifts (δ values) of all the protons, varying from 0.1 p.p.m. for the meso protons through 0.07—0.08 p.p.m. for the nuclear methyl protons to zero for the methyl ester. These non-specific shifts are characteristic of porphyrins and are simply due to an averaging of the macrocyclic ring current over the surface of the molecule. Essentially, averaging of the ring current of one molecule at a neighbouring molecule in solution produces a high-field shift even at low dilutions. This has been described previously.[2] We report here the chemical shifts from the 0.7 mM solution as essentially infinite dilution values. It is of more interest to consider why this nickel porphyrin shows no aggregation effects, while the not very dissimilar nickel(II) 2-vinylphyllorerythrin methyl ester (**1**) showed pronounced aggregation effects down to very low concentrations (< 1 mM). Aggregation must involve the central nickel(II) atom and therefore is presumably due to the co-ordination unsaturation of the nickel in the axial direction. In (**1**) this co-ordination unsaturation could be relieved by co-ordination with the oxygen atoms of the conformationally mobile propionate ester side-chain and still allow the porphyrin planes to be planar, the optimum arrangement. This is not possible in (**2**) as both donor groups, *i.e.* the γ-keto and C-6 methoxycarbonyl, are directly attached to the porphyrin nucleus and unable to co-ordinate to the nickel atom of a neighbouring molecule and still form a parallel plane aggregate.

The assignments of the nickel(II) porphyrin given were confirmed by nuclear Overhauser enhancement (n.O.e.) experiments. Irradiating the low-field (δ 3.59) methyl group gave a n.O.e. at one meso proton (δ 9.80), whereas irradiation of CH_2 of the C-2 and C-4 ethyl groups, which are almost isochronous at δ 1.74, gave a n.O.e. at the two meso protons resonating at δ 9.66 and 9.80. This unambiguously identifies the three meso protons and the C-5 methyl group. The assignments of the remaining nuclear methyl groups and of the C-2 and C-4 ethyl groups are not known, but as the chemical shifts of the protons in each group are virtually identical (±0.01 p.p.m.) this is of no consequence.

The geometry of the molecules considered was taken from molecular models and *X*-ray studies of related molecules. The porphyrin (**2**) was assumed planar, except for the *exocyclic* ring which was taken as an envelope conformation with C-7β out of the molecular plane by about 0.4 Å. In the chlorin (**3**) ring D was assumed to be similar to the known conformation of ring D in the chlorophyll system,[10] with an equatorial C-7α disposition which results in a preferred half-chair conformation for the *exocyclic* ring, with C-7β essentially in the plane of the macrocycle. The geometries of the isobacteriochlorins (**4**) and (**5**) were derived from the chlorin geometry with the extra reduced pyrrole rings in half-chair conformations, as was found in nickel(II) octaethylisobacteriochlorin.[11] From previous studies we may safely assume *cis* substitution,[11,12] and this results in one substituent in each pyrrole ring being pseudo-axial and one pseudo-equatorial, but which is the preferred orientation, if any, is not known at the present time. *X*-Ray studies may not necessary be unequivocal here as there is the possibility of more than one conformation of very similar energy.

The precise geometries of the hexa- (**6**) and (**7**) and octa- (**8**) hydroporphyrins are not known, and may indeed be quite non-planar with the four nitrogens coplanar, as has been found for all the nickel(II) hydroporphyrins.[9] In practice this is of less importance than may have been anticipated as it can be safely assumed that the non-reduced pyrrole rings A and B will form an approximately planar moiety with the nickel atom. Thus, the chemical shifts of the protons on these subunits may be utilised to deduce the ring currents in these molecules; the remaining proton chemical shifts will be more affected by conformational changes, and indeed are so remote from the area of the ring current as not to experience significant ring current shifts.

Because of the unavoidable uncertainties in the geometries of the reduced porphyrins it is more convenient to compare directly the observed chemical shifts of the protons in the reduced porphyrins with those calculated from the corresponding protons in the nickel(II) porphyrin (**2**), rather than giving observed and calculated shift differences, as previously.[5,7] This is obviously an entirely equivalent calculation as the calculated chemical shift (δ_{HP}) of any proton in the hydroporphyrin is given from that of the correponding proton in the porphyrin (δ_P) by equation (2), where Δ_P is the calculated

$$\delta_{HP} = \delta_P - (\Delta_P - \Delta_{HP}) \qquad (2)$$

ring current shift in the porphyrin and Δ_{HP} is the calculated ring current shift in the hydroporphyrin. The only exception to this is where there are no chemically equivalent protons in the porphyrin, *e.g.* 7-H and 8-H, and in this case the base molecule is taken as the chlorin (**3**).

Apart from the porphyrin, in which the assignments of the protons in the *exocyclic* ring are reasonably straightforward (though even here decoupling was necessary to identify the overlapping 2- and 4-methylene resonances from 7-CH_2 resonances), the assignments of the protons in the *exocyclic* ring are not known. They form a complex four-spin system as the chemical equivalence found in the porphyrin is destroyed by the additional chirality at C-7 in the reduced porphyrins. Thus, they are not recorded here.

Results and Discussion

The observed and calculated [from equation (2)] proton chemical shifts of the compounds investigated are given in Tables 1 and 2. Most of the spectra were assigned with the aid of a number of n.O.e. and decoupling experiments reported previously.[8] Where the assignments given are not unequivocal is indicated in the Tables, though the ring current calculations do assist in clarifying some of the provisional assignments reported previously.

Table 1. Observed and calculated proton chemical shifts (δ p.p.m.) of nickel(II) anhydrorhodoporphyrin XV methyl ester (**2**) and the analogous chlorin (**3**) and isobacteriochlorins (**4**) and (**5**)

Proton		Ni porphyrin[a] (2)	Ni chlorin (3)		Ni isobacteriochlorins (4)		(5)	
			obs.	calc.[d]	obs.	calc.[d]	obs.	calc.[d]
	α	9.66	8.61[b]	8.63	8.06	7.78	6.94	7.18
meso	β	9.80	8.86[b]	8.77	7.00	7.32	8.10	7.93
	δ	9.63	7.62[b]	7.98	7.02	7.15	6.44	6.63
	C-1	3.40	2.84[b]	2.89	2.57	2.61	1.00	
β-Me	C-3	3.40	2.97[b]	2.98	2.68	2.68	2.52[b]	2.61
	C-5	3.59	3.18[b]	3.15	1.69		2.86[b]	2.87
	C-8	3.42	2.01		1.74	1.74[c]	1.70	1.68[c]
C-2a	CH_2	3.85	3.40	3.39	3.12	3.11	1.90	
							2.25	
C-2b	Me	1.74	1.50	1.52	1.39	1.36	1.25	1.15
C-4a	CH_2	3.85	3.40	3.42	3.00	3.04	3.10	3.11
C-4b	Me	1.73	1.53	1.53	1.29	1.32	1.36	1.36
C-6	OMe	4.18	4.05	3.99	3.66	3.70	3.92	3.87
C-7	H		3.67		3.28	3.19[c]	3.27	3.24[c]
C-8	H		4.00		3.50	3.50[c]	3.45	3.44[c]

[a] C-7α-, C-7β-CH_2, 4.07, 3.71. [b] Assignments may be interchanged. [c] Chlorin as reference, see text. [d] Porphyrin μ_P 16.1, μ_H 18.1; chlorin μ_P 13.0, μ_H 13.4; isobacteriochlorin μ_P 13.0, μ_H 7.5.

Table 2. Observed and calculated proton chemical shifts (δ, p.p.m.) of nickel(II) hexahydro- (**6**), (**7**) and octahydro- (**8**) porphyrins

Proton		Observed shifts: Ni hexahydro (6)	(7)	Ni octahydro (8)	Calculated shifts: a	b
	α	6.75	6.79	6.69	6.51	6.73
meso	β		5.87		6.00	5.92
	δ	5.84			6.17	6.09
β-Me	C-1	2.05	1.92[c]	1.85[c]	2.15	2.06
	C-3	2.15	2.16	2.10	2.20	2.16
C-2a	CH_2	2.58	2.62	2.50	2.62	2.57
C-2b	Me	1.13	1.11	1.08	1.13	1.13
C-4a	CH_2	2.30[c]	2.48	2.22[c]	2.56	2.47
C-4b	Me	1.00	1.09	0.95	1.10	1.10

[a] μ_P 10.0, μ_H 0.0. [b] μ_P 7.0, μ_H 6.0. [c] Shifts not directly comparable due to conformational changes.

Observed proton chemical shifts for the nickel(II) porphyrin (**2**) are all close to the values recorded previously for the similarly substituted zinc(II) phylloerythrin methyl ester,[7] and there is thus no reason to assume that the macrocyclic ring current is any different in (**2**). We therefore use the same values of the equivalent dipoles for (**2**) as were previously found for phylloerythrin (**1**).

Nickel(II) anhydrorhodochlorin methyl ester (**3**). The proton chemical shifts in the chlorin can now be calculated directly from those of (**2**) using equation (2), provided the appropriate values of the equivalent dipoles are known. Two different calculations were attempted. In the first, following previous calculations for the chlorin ring,[4b,7] only one value of the inner loop dipole was used. In the second calculation two values were incorporated, reflecting the molecular symmetry of the chlorin (*i.e.* one value for A-B and B-C, another value for C-D and D-A). The agreement between observed and calculated shifts was not significantly improved in the latter case, so in Table 1 only the results of the original, simple calculation are given. Inspection of the results shows the generally good agreement obtained; only for the δ-meso proton does the calculated differ significantly from the observed value. This *may* be due to the different effect of the C-10 keto group on this proton in the two compounds, but it has been noted previously[7] that there is an additional upfield shift of about 0.2—0.3 p.p.m. on a meso proton next to the reduced pyrrole ring. This could be due to the relief of the β-methyl/*meso* H steric interaction in the porphyrin, or to the removal of the anisotropic contribution from the pyrrole double bond. This additional upfield shift is observed here for the δ-meso proton. However, for those protons for which substituent and hybridisation effects should be minimal, *i.e.* the protons on the β-side-chains, there is essentially exact agreement between the observed and the calculated shifts, which is encouraging.

The values of the inner loop dipoles found for (**3**) are somewhat lower than those found previously for zinc(II) methylpyropheophorbide *a* (μ_P 14.6, μ_H 16.5),[7] and this is very likely due to the influence of the nickel atom in perturbing the chlorin macrocycle. This is illustrated by the comparison of the proton chemical shifts of (**3**) with those of the corresponding free base. The shift differences (free base–nickel complex) for the meso and β-methyl protons are 0.60, 0.51, 0.66 (α, β, δ) and 0.32, 0.21, 0.30, and 0.22 (C-1, -3, -5, -8). These show clearly the considerable perturbing effect of the nickel atom in the series, and also show that there is no differential complexation at different regions of the macrocycle, in support of our conclusion

that there is no evidence to suggest that an unsymmetrical inner loop model is required for this system.

Nickel(II) *isobacteriochlorins* (**4**) *and* (**5**). The proton chemical shifts in these compounds were also calculated using equation (2), directly from the corresponding proton shifts of the porphyrin (**2**), except for 8-Me and 7-H and 8-H for which the chlorin (**3**) was used as the reference compound. Following the results for the chlorin above, only one value of the inner ring dipoles was used, and the best fit of the calculated and observed results is given in Table 1. The agreement between the observed and calculated shifts is only fair for the meso protons, and again a consistent upfield shift due to the release of the β-methyl steric effects of about 0.2—0.3 p.p.m. is observed for meso protons adjacent to the reduced pyrrole subunits. However, once again for those protons for which substituent and hybridisation changes are minimal, *i.e.* the side-chain protons, there is essentially complete agreement between observed and calculated shifts. Even for those protons for which the nickel chlorin is the reference compound there is very good agreement with the observed shifts, which is quite encouraging. The values of the equivalent dipoles obtained for the isobacteriochlorins are almost identical with those found in the reduced phylloerythrin system (μ_P 13.6, μ_H 7.5).[7] The contrast with the chlorin results given earlier is simply due to the fact that the isobacteriochlorins derived from the phylloerythrin nucleus (**1**) were also the nickel complexes. This is of some interest as it clearly demonstrates that the values of the equivalent dipoles can be transferred to chemically similar molecules. However, it raises the question as to what effect the nickel atom has on the macrocyclic ring current in the isobacteriochlorin and the bacteriochlorin system. In reference 7 the reduced inner loop ring current in the isobacteriochlorin, as compared to the bacteriochlorin, system was attributed to an increase in the ring deformation with two adjacent dihydropyrrole subunits. This deformation of the macrocycle is very probably enhanced by the central nickel atom in the isobacteriochlorins, whereas the only data in the bacteriochlorin system available to us were for bacteriochlorophyll *a*, in which the central magnesium atom has much less tendency to deform the macrocycle.

Nickel(II) *hexahydro-* (**6**), (**7**) *and octahydro-* (**8**) *porphyrins*. The proton chemical shifts of these molecules may also be calculated directly from those of the nickel(II) porphyrin (**2**) using equation (2), though for these molecules the observed data is less complete and the calculated values are less unequivocal. The proton spectra of these molecules have only been partially assigned,[8] as there is a spectral region (δ 2.2—2.8) in which many of the ring protons and the side-chain methylenes absorb, forming a complex overlapping pattern. Also, the molecules are very likely non-planar and the conformational changes consequent upon the rehydridisation of some of the meso carbon atoms make any deduction of ring current shifts in these saturated regions of the molecules questionable. Thus we consider only that region of the molecule adjoining the unreduced A and B pyrrole rings. Even so, there are a number of assigned protons in this region and the observed and calculated shifts are given in Table 2.

Two different calculations were performed in this case. (Note that the molecular symmetry is such that only one ring current calculation is required for all three molecules.) In the first calculation the equivalent dipoles of the pyrrole subunits A and B were adjusted to give the best agreement with the observed shifts without including any inner loop ring current. In the second calculation an inner loop ring current circulating between the nickel atom and the two pyrrole rings was included, together with the pyrrole ring dipoles.

The results (Table 2) are of some interest. Again we note the extra high-field shift of a meso proton adjacent to a reduced subunit [*e.g.* the δ-meso proton in (**6**)], but the remaining calculated shifts are in very reasonable agreement with the observed values. The agreement between the observed and calculated shifts is however significantly better for the second model, in which apart from the δ-meso proton, there is essentially complete agreement between the observed and calculated shifts. In Table 2 those shifts in which extraneous substituent effects are likely to occur have been labelled. For example, the C-1 methyl of (**7**) has the steric interaction between the pyrrole β-methyl and the δ-meso proton removed, due to the reduction at the δ position, and this would be expected to give a small upfield shift of this methyl group. This is exactly what is observed (Table 2).

The results in Table 2 indicate that the nickel atom does participate in a circulating π-electron loop. However, the differences between the two calculated data sets are not so great as to be absolutely definitive over this conclusion, particularly in view of possible deformations of the macrocycle around the A-B rings. Note that only one inner loop hexagon was included in the calculations, though formally three inner loops could be included for the hexahydroporphyrins and two for the octahydroporphyrin. The present data would not justify these more complex models. The additional current loops are so far removed from the protons under consideration that there would be only very small ring current shifts; the likely deformation of the macrocycle from a planar entity which would be expected to be most pronounced in this part of the molecule would not favour any circulating π-electrons, and the agreement between the observed and calculated shifts with the second model is so good that there is no justification for a more complex parameterisation.

Conclusions

The analyses of the proton chemical shifts of this series of nickel porphyrin (**2**) and reduced analogues (**3**)—(**8**) both confirm and expand previous studies in this area. The disturbing effect of nickel on the inner loop ring current in the chlorin series is very clearly identified, the inner loop current decreasing by about 20% from the corresponding zinc(II) and magnesium(II) chlorins. Conversely, the nickel(II) isobacteriochlorins (**4**), (**5**) examined here show precisely the same ring currents as the nickel isobacteriochlorins derived from the phylloerythrin (**1**), showing that in these systems the perturbing effects on the inner loop ring current of the C-9 keto function and the γ-keto function are very comparable.

The proton chemical shifts in the nickel(II) hexa- (**6**), (**7**) and octa- (**8**) hydroporphyrins are best accounted for by the inclusion of a small inner loop ring current in one quadrant of the macrocycle, together with the pyrrole ring currents. This intriguing result would need to be further substantiated before it could be regarded as definitive.

Experimental

Proton n.m.r. spectra were measured at 360 MHz on a Nicolet NT-360 spectrometer and at 250 MHz on a Bruker WM250 spectrometer. Chemical shifts (δ) are reported relative to $CHCl_3$ at 7.260 p.p.m. Typical conditions were: probe temperature 23 °C, 16 or 32 K data points, sweep width 4 kHz giving a digitisation accuracy of 0.25 or 0.5 Hz/point, pulse width 7 μs, acquisition time 1 or 2 s, and *ca.* 80 accumulations. M.p.s are uncorrected and were measured on a Thomas/Bristoline hot stage. Electronic absorption spectra were measured on a Hewlett-Packard 8450A spectrophotometer. The elemental analysis was performed at the Microchemical Analysis Laboratory, U.C. Berkeley. Reactions were monitored using thin-layer chromatography on commercially available Eastman-Kodak 13181 (100 μm thick) silica gel sheets. Prepar-

ative thick-layer chromatography was carried out on 20 × 20 cm glass plates coated with Merck GF 254 silica gel (1 mm thick). Gravity and flash colomn chromatography employed either Merck neutral alumina (70—230 mesh) or Merck silica gel 60.

Anhydromesorhodoporphyrin XV *methyl ester.* Zinc(II) anhydromesorhodochlorin XV methyl ester [8] (5.82 mg) in dry chloroform (2 ml) was treated with dichlorodicyanobenzoquinone (2.21 mg) in dry benzene (1 ml) at room temperature. Spectrophotometry showed complete conversion of chlorin into porphyrin, so the solution was applied directly to an alumina column (Brockmann Grade III, elution with 5% methanol in dichloromethane). The major green band was collected, evaporated to dryness, taken up in dichloromethane (50 ml), and then shaken vigorously with 10% aqueous HCl (50 ml). Upon washing the organic layer with water the colour changed from green to red, and the organic phase was dried (Na_2SO_4) and evaporated to dryness to give a solid which was subject to thick-layer chromatography on silica gel eluting with 2% methanol in dichloromethane. The major red band yielded the *title compound* (5.2 mg, 85%), m.p. > 300 °C (Found: C, 73.9; H, 10.4; N, 6.65. $C_{33}H_{34}N_4O_3$ requires C, 74.13; H, 10.48; N, 6.41%); δ($CDCl_3$) 10.171, 9.993, and 9.947 (each 1 H, s, meso-H), 4.260 and 3.945 (each 2 H, t, exocyclic ring CH_2), 4.207 (3 H, s, OMe), 4.068 and 3.966 (each q, 2 H, 2- and 4-CH_2Me), 3.73, 3.61, 3.60, and 3.53 (each 1 H, s, 1-, 3-, 5-, 8-Me), 1.86 and 1.83 (each 3 H, t, 2- and 4-CH_2*Me*), and −3.00 (2 H, br s, NH); $\lambda_{max.}$(CH_2Cl_2) 408 (ε 130 000), 518 (9 800), 558 (12 400), 582 (10 000), and 640 nm (8 800).

Nickel(II) *anhydromesorhodoporphyrin* XV *methyl ester* (**2**). The foregoing porphyrin in chloroform (5 ml) was treated with saturated nickel(II) acetate in methanol (5 ml). The solution was heated under reflux until spectrophotometry indicated complete metallation (18 h), and was then diluted with dichloromethane, washed with water (2 × 50 ml), dried (Na_2SO_4) and evaporated to dryness. The residue was chromatographed on a silica gel column (elution with 4% tetrahydrofuran in dichloromethane) and the major green band was collected to give the title compound, m.p. > 300 °C; $\lambda_{max.}$ 406 (ε 124 000), 550infl. (8 000), and 588 nm (24 800).

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