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NMR studies of nonplanar porphyrins. Part 2. Effect of nonplanar conformational distortions on the porphyrin ring current

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The ring currents in the sterically congested and highly nonplanar porphyrin complexes 1a and 2a have been investigated using a double-dipole model of the porphyrin ring current effect. The equivalent dipoles needed to simulate the ring current in the saddle-shaped complex 1a were indistinguishable from those previously determined for the planar or nearly planar complex 3a. A 5% decrease in the equivalent dipoles was required to reproduce the ring current shifts in the ruffled complex 2a. The extremely large nonplanar conformational distortions seen for the porphyrin macrocycles in complexes 1a and 2a thus seem to cause little decrease in the porphyrin ring currents measured by this empirical model.

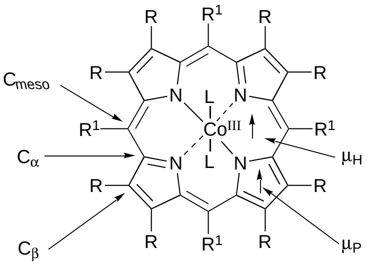
Introduction

The anomalous magnetic properties of cyclic conjugated π-systems compared to acyclic analogues have been known for some time, and have been explained using both classical[1] and quantum mechanical[2] models in terms of a ring current effect. A broader interest in this phenomenon emerged with the discovery that the ring current effect could be used to rationalize the different proton NMR chemical shifts of benzene and acyclic olefins.[3] Interest in the ring current effect continues unabated, as evidenced by recent studies of the ring currents in benzene,[4] C_{60},[5] cyclophanes,[6] porphyrins[7] and expanded porphyrins.[8]

In the case of the biologically important porphyrins, empirical ring current models have been very successful in probing porphyrin aggregation[9] and ligand binding phenomena.[10,11] Ring current decreases associated with reduction of the porphyrin macrocycle have also been the subject of detailed studies.[12] However, to the best of our knowledge the effect of nonplanarity on the porphyrin ring current has never been thoroughly investigated. Interestingly, several studies of highly substituted porphyrins have indicated that nonplanar distortions produce measurable decreases in the porphyrin ring current effect.[13]

Recently, porphyrins which adopt extremely nonplanar conformations in the crystalline state and in solution have been synthesized by crowding the porphyrin periphery with substituents (*e.g.* **1**)[14,15] (Fig. 1) or by incorporating very bulky substituents at the *meso* positions (*e.g.* **2**).[16] These porphyrins seemed well suited for determining the effect of nonplanarity on the porphyrin ring current. Accordingly, in Part 1 of this series[17] we prepared complexes **1a–f** and **2a–f** and used molecular mechanics calculations and proton NMR spectroscopy to obtain the structural and chemical shift data necessary to investigate the ring currents in these systems. Complexes **1a** and **2a** were chosen for study because the ring current parameters for complex **3a**, which does not have peripheral steric crowding and so has a planar or nearly planar conformation of the porphyrin macrocycle, have already been determined.[10b]

The ring currents in complexes **1a** and **2a** are investigated with the same double-dipole model[9,10,13] used to probe the ring current in complex **3a**.[10b] In this model, the current loops of the porphyrin π-electrons are simulated by dipoles (μ) located at the centre of the pyrrole rings (μ_P) and hexagon rings (μ_H) (Fig. 1). Two sets of dipoles ('double dipoles') are located 0.64 Å above and 0.64 Å below the plane of the porphyrin to represent the current loops of the π-electrons. The ring current shift for nucleus R (δ_R) in a porphyrin is calculated using an expanded version of the standard dipole equation (1). In this case, *r* is the



1 R = CH_2CH_3, $R^1 = C_6H_5$, M = 2H
2 R = H, $R^1 = C(CH_3)_3$, M = 2H
3 R = H, $R^1 = C_6H_5$, M = 2H
4 R = CH_3, $R^1 = C_6H_5$, M = 2H
a M = Co^{III}, L = pyridine
b M = Co^{III}, L = 3-phenylpyridine
c M = Co^{III}, L = 3-chloropyridine
d M = Co^{III}, L = 1-methylimidazole
e M = Co^{III}, L = 4-phenylimidazole
f M = Co^{III}, L = 4-methylpiperidine
5 R = R^1 = H, M = 2H
6 R = $R^1 = C_6H_5$, M = 2H
7 R = CH_2CO_2H, $R^1 = C_6H_5$, M = Ni^{II}

Fig. 1 Structures and nomenclature for the porphyrins discussed in this study

$$\delta_R = \sum_{i=1,8} \mu_H(1 - 3\cos^2\theta/r^3) + \sum_{i=1,8} \mu_P(1 - 3\cos^2\theta/r^3) \quad (1)$$

distance of the nucleus from the dipole and θ is the angle made by the nucleus, the dipole and the *z* axis orthogonal to the current loop.

The double-dipole model is well suited for determining the effect of nonplanarity on the porphyrin ring current because it is possible to reorientate the dipoles to simulate current loops for pyrrole and hexagon rings that are no longer in the porphyrin plane. For example, the crystal structures of **1** (M =

Table 1 Chemical shifts, ring current shifts and calculated ring current shifts for **1a**, **2a** and**3a**

					Ring current shifts (Δ*δ*)					
		Chemical shifts (*δ*)			**1a**		**2a**		**3a**	
		1a	**2a**	Ref.[a]	(Obs.)	Calc.	(Obs.)	(Calc.)	(Obs.)	(Calc.)
Pyridine	*para*	6.21	6.36	8.06	−1.85	−1.75	−1.70	−1.62	−1.74	−1.74
	meta	5.27	5.24	7.49	−2.22	−2.34	−2.25	−2.28	−2.31	−2.34
	ortho	2.56	2.00	8.24	−5.68[b]	−6.21	−6.24	−6.20	−7.43	−7.37
meso	*ortho*	8.16		7.47	0.69	0.69			0.73	0.87
	meta	7.71		7.30	0.41	0.48			0.45	0.54
	para	7.76		7.30	0.46	0.46			0.45	0.54
	Bu^t		1.49	0.94			0.55	0.61		
Pyrrole	CH_2	2.23		2.06	0.17	0.16[c]				
	Me	−0.05		1.00	−1.05	−1.15[c]				
	β-H		9.22	6.05			3.17	3.66		
1/2/3	NH	−2.0	+1.58[d]	6.8	−8.8	−8.78	−5.22[d]	−10.3	−9.55	−9.53
4a	Me	1.99		1.54[e]	0.45	0.40				
Co^{III}–N$_{ligand}$/Å						1.98		1.98		1.98
μ_P/Å^3						18.6		17.7		18.6
μ_H/Å^3						20.8		19.7		20.8
b						−0.31		−0.485		−0.485
h/Å						3.80		3.67		3.67

[a] See text. [b] These protons may be subject to an additional downfield shift due to their proximity to the porphyrin nitrogen atoms (see text). [c] Shifts given are for a mixture of 60% axial and 40% equatorial ethyl groups (see text). Note that the methylene protons are diastereotopic at 223 K when macrocyclic inversion is slow on the NMR timescale. In this case, the chemical shift difference of the methylene protons obtained from the ring current calculations (1.07 ppm) is larger than but in qualitative agreement with the measured shift difference of 0.55 ppm. [d] The NH protons in **2** show an unusual downfield shift which is not due to a change in the porphyrin ring current effect (see text). [e] Reference compound was *cis*-butene.[19c]

Ni^{II},[14b] Co^{II},[15b] Cu^{II}[15b] and Zn^{II}[14a]), the calculated minimum energy structures for these complexes,[15b] and the calculated minimum energy structure of **1a** (see Fig. 2 of the preceding paper) all show a saddle[18] conformation of the porphyrin macrocycle. In this conformation, alternate pyrrole rings of the porphyrin macrocycle are tilted up and down with respect to the plane of the porphyrin core atoms. The double-dipole program can be modified to calculate ring current shifts in this distorted system by moving the current loops of the pyrrole rings out of the porphyrin plane and tilting them at an angle to the plane, and by rotating the current loops of the hexagon rings with respect to the porphyrin plane.

The crystal structure of **2** (M = Zn^{II}),[16b] the calculated minimum energy structure of **2** (M = Ni^{II}),[16c] and the calculated minimum energy structure of **2a** (see Fig. 3 of the preceding paper) show a different conformation of the porphyrin macrocycle. In this case, the macrocycles adopt ruffled[18] conformations in which alternate pyrrole rings of the porphyrin are twisted clockwise or anticlockwise about the M–N bond. The ring current in this system can also be simulated using the double-dipole model. The hexagon current loops can be moved out of the porphyrin least-squares plane and tilted at an angle to the plane, and the pyrrole current loops can be rotated with respect to the porphyrin plane. The current loops of other aromatic substituents such as the *meso* phenyl groups in **1a** and the axial pyridine ligands in **1a** and **2a** can also be simulated by dipoles included in the calculations.

Results and discussion

Determination of the ring current parameters for 1a and 2a

The ring current shifts used to determine values for the pyrrole and hexagon dipoles were obtained from the proton chemical shifts in complexes **1a** and **2a** and a series of reference compounds (Table 1). The reference compounds used for the phenyl and ethyl protons in **1a** were α-methyl styrene and butene.[10d] For **1b**, the pyrrole protons were referenced to pyrrole[19a] and the *tert*-butyl protons to neopentane.[19b] The pyridine ligand protons were referenced to the pyridine protons in a cobalt(III) complex with dimethylglyoxime.[10b] Finally, an approximate ring current shift for the porphyrin NH protons was obtained from the chemical shift of the NH proton of pyrrole at infinite dilution.[10d]

X-Ray crystal structures of **1a** and **2a** were not available for use in the ring current calculations. The macrocycle geometry for **1a** was therefore taken from the crystal structure of **1** (M = Co^{II}),[15b] which was very similar to the calculated minimum energy of **1a**.[17] The macrocycle geometry for **2a** was taken from the calculated minimum energy structure of this complex.[17] Molecular modelling studies in Part 1 of this series[17] also indicated a negligible change in the Co^{III}–N$_{ligand}$ distance for complexes **1a**, **2a** and **3a** (1.997 ± 0.003 Å), therefore the Co^{III}–N$_{ligand}$ distance (1.98 Å) and pyridine ligand geometry used in the calculations were those previously described for **3a**.[10b]

A significant difference between the structures of complexes **1a**, **2a** and **3a** is the orientation of the axial ligands, which, as shown in Part 1 of this series,[17] is dependent upon the conformation adopted by the nonplanar porphyrin. In both **1a** and **2a**, the planes of the axial ligands in the calculated minimum energy structures are orientated essentially parallel to cavities formed by the saddled or ruffled macrocycles (see Figs. 2 and 3 of the preceding paper). For the ring current studies, idealized forms of these structures were used, with the pyridine ligands being orientated exactly parallel to the porphyrin cavities to give angles between the ligand planes and theCo^{III}–N$_{porphyrin}$ bonds of 0° for **1a** and 45° for **2a**.

The double-dipole program (DCALC7) was then modified to allow the equivalent dipoles for the pyrrole and hexagon current loops to be reorientated. For **1a**, the tilt and rotation angles of the pyrrole and hexagon current loops were determined from the crystal structure of **1** (M = Co^{II}).[15b] The tilt angle of the pyrrole current loops was 27.6°, the rotation angle of the hexagon current loops was taken as 15° [an average of the dihedral angles between the N$_{porphyrin}$–Co^{III}–N$_{porphyrin}$ and porphyrin planes (7.5°) and the C$_\alpha$–C$_{meso}$–C$_\alpha$ and porphyrin planes (22.5°)], and the out of plane displacement of the pyrrole rings was found to be 0.68 Å. For complex **2a**, the tilt angle (17.2°) and displacement (0.63 Å) of the hexagon current loop, and the average rotation angle of the pyrrole current loops (25.2°) were determined from the calculated minimum energy structure of this complex.[17]

Additional modifications were made to the ring current program so that the current loops of the aromatic substituents and ligands in **1a** and **2a** could be simulated. First, the current loops for the *meso* phenyl rings (μ = 27.6 Å^3)[10b] were rotated relative to the porphyrin least-squares plane so as to match the average angle seen in the crystal structure of **1** (M = Co^{II}).[15b] The ring currents of the axial ligands in **1a** and **2a** were also simulated with the same dipole used for the *meso* phenyl rings (27.6 Å^3).

Ring current calculations for complexes **1a** and **2a** were then undertaken using the new double-dipole model. The calculated ring current shifts for the phenyl and ethyl protons of **1a**, the pyrrole and *tert*-butyl protons of **2a**, and the pyridine *meta* and *para* protons of both complexes are only a function of the dipoles μ_P and μ_H, so they provide a good measure of the porphyrin ring current effect. To determine if the ring current was different in **1a** and **2a** than in **3a**, ring current shifts were initially calculated with the same dipoles used to simulate the ring current of **3a** (μ_P = 18.6 Å^3 and μ_H = 20.8 Å^3).[10b]

For complex **1a**, good agreement was obtained between the observed ring current shifts and those calculated using the dipoles for **3a** (Table 1), suggesting that the ring currents in these porphyrins are similar. It is worth noting that poor agreement was initially obtained for the ethyl protons until a mixture of two ethyl orientations was included in the model. These orientations had the ethyl groups in axial positions, as shown in Fig. 2 of the preceding paper, and in equatorial positions where the methyl of the ethyl group was rotated approximately 180° about the C_β–CH_2 bond. Previous molecular modelling studies of **1** (M = Co^{II})[15b] have shown that there is only a small energy difference between porphyrins with axial and equatorial orientations of the ethyl groups.[15c] The best agreement between the observed and calculated shifts was obtained for a mixture of 60% axial and 40% equatorial ethyl groups, and the calculated shifts given in Table 1 are for this mixture. Additional evidence in support of an axial–equatorial conformational equilibrium of the ethyl groups in **1a** was obtained from complex **4a**, where there was excellent agreement between the observed and calculated ring current shifts for the methyl groups bonded directly to the pyrrole rings (Table 1).

For complex **2a**, the agreement between the observed and calculated ring current shifts could be improved if the dipoles were decreased by 5% from the values previously determined for complex **3a**, giving μ_P = 17.7 Å^3 and μ_H = 19.7 Å^3. The observed and calculated ring current shifts using the revised dipoles are given in Table 1. The smaller dipoles for **2a** suggest that the ring current is slightly less than that in **3a** and **1a**. The chemical shift changes seen for **2a** could also be due to an increase in the Co^{III}–N_{ligand} distance rather than a change in the ring current effect, although the similar Co^{III}–N_{ligand} distances calculated for **1a**, **2a** and **3a** in Part 1 of this series[17] argue against this being the case.

An attempt was made to relate the small ring current decrease seen for **2a** to structural differences between complexes **1a**, **2a** and **3a**. Any reduction in the ring current effect due to nonplanarity is probably due to a disruption in the conjugation pathway at the *meso* positions of the porphyrin macrocycle. The resonance integral (β) between the C_α and C_{meso} carbon atoms would seem to be an appropriate measure of this disruption. The reduction in β compared to the standard resonance integral (β_0) in nonplanar π-systems varies according to the cosine of the C–C torsion angle (θ) [eqn. (2)].[20]

$$\beta = \beta_0 \cos\theta \qquad (2)$$

A decreased ring current in **2a** compared to **1a** suggests larger deviations of the N–C_α–C_{meso}–C_α and C_β–C_α–C_{meso}–C_α torsion angles from planarity (0° and 180°, respectively), and this is indeed found to be the case. In the crystal structure of **1** (M = Co^{II}),[15b] the average N–C_α–C_{meso}–C_α and C_β–C_α–C_{meso}–C_α torsion angles are 17.8° and 170.0°. Similar values are obtained from the calculated minimum energy structure of **1a**. In contrast, the torsion angles in the calculated minimum energy structure of **2a** show much larger deviations from those expected for a planar system, with average N–C_α–C_{meso}–C_α and C_β–C_α–C_{meso}–C_α torsion angles of 27.5° and 148.5°, respectively. Using eqn. (2), the C_α–C_{meso} torsion angles yield resonance integrals that are decreased by 1.5–4.8% for **1a** and 11.3–14.7% for **2a**. These decreases are somewhat larger than those measured experimentally, but they are in qualitative agreement with the ring current changes determined using the double-dipole model.

Protons inside the close range limit

The dipole approximation breaks down for the pyridine *ortho* protons and for the NH protons of the free base porphyrins because they are close to the current loops. Therefore, the ring current shifts for these protons are calculated using a close range approximation.[10b] This approximation calculates shifts within a cylinder of height (h) and a radius given by the porphyrin current loop. The shift for a nucleus R, which is z Å from the plane of the porphyrin, is obtained by extrapolation of the shift (δ_h) and gradient (g_h) at the top of the cylinder using a polynomial function given in eqn. (3), where c is defined in eqn. (4).

$$\delta_R = \delta_h + g_h[b(h^2 - z^2) + c(h^4 - z^4)] \qquad (3)$$

$$c = -(1 + 2bh)/4h^3 \qquad (4)$$

The parameters b and h are derived from experimental data, namely the ring current shifts of the pyridine *ortho* and NH protons. The ring current shifts for the NH protons are calculated from the macrocycle geometries of the cobalt(III) complexes by adding a hydrogen atom to the porphyrin nitrogen atoms using an N–H bond length of 1.00 Å.[21] The constant c is calculated from the requirement for second-order continuity at the boundary. The values of b and h previously determined for **3a** are −0.485 Å^{-2} and −3.67 Å, respectively.[10d]

When the close range parameters for **3a** were used to calculate the ring current shifts in **2a**, excellent agreement was obtained with the observed ring current shift of the pyridine *ortho* protons (Table 1). However, there was a large discrepancy between the observed and calculated ring current shifts for the NH protons in **2** because of the unusual downfield shift of these protons (+1.58 ppm). The assignment of the NH protons was therefore confirmed by additional NMR studies. The ^{1}H NMR spectrum of **2** was measured in C_6D_6, where the water protons (0.40 ppm) and NH protons (2.70 ppm) were better separated than in $CDCl_3$. The signal assigned to the NH protons could then be integrated, and was found to be two protons compared to eight protons for the pyrrole protons. Cooling a solution of **2** in CD_2Cl_2 to 193 K also caused a small upfield shift of the signal assigned to the NH protons, behaviour which is typical of porphyrin NH protons. The signal assigned to the porphyrin NH protons again integrated to two protons, compared to 36 protons for the *tert*-butyl groups. As far as we are aware, the chemical shift of the NH protons in **2** is the most downfield of any porphyrin reported to date.

Other *meso*-*tert*-butyl substituted porphyrins were prepared[22] to see if the NH protons in these systems also showed downfield shifts. The NH proton of 5,15-di(*tert*-butyl)porphyrin in $CDCl_3$ was seen at −0.95 ppm.[22a] This is close to the average chemical shift of −1.09 ppm for the NH protons in **2** (+1.58 ppm) and porphyrin **5** (−3.76 ppm),[23] indicating a substituent effect of the *tert*-butyl group. This hypothesis was supported by the chemical shift of the NH protons in 5-*tert*-butylporphyrin (−2.64 ppm),[22b] which is similar to the weighted chemical shift obtained from **2** and **5** (−2.42 ppm). At present, the origin of this substituent shift is unknown, although the similar chemical shifts of the pyrrole hydrogens in **2a** (9.22 ppm) and **2** (9.07 ppm) show that it is not due to a decrease in the ring current of the free base porphyrin **2**.

Table 2 Chemical shifts, ring current shifts and calculated ring current shifts for the ligand protons in **1d**, **2d** and **3d**

	Chemical shifts			Ring current shifts					
	1d	**2d**	Ref.[a]	**1d**	Calc.	**2d**	Calc.	**3d**	Calc.
Me	2.18	2.25	3.81	−1.63	−1.63	−1.56	−1.55	−1.67	−1.66
H-2	2.44	1.86	7.39	−4.95[b]	−5.70	−5.53	−5.44	−6.71	−6.65
H-4	1.99	1.40	6.70	−4.71[b]	−5.59	−5.30	−5.42	−6.52	−6.55
H-5	4.76	4.88	7.08	−2.32	−2.31	−2.20	−2.13	−2.24	−2.31
$Co^{III}–N_{ligand}$/Å					1.98		2.08		1.93

[a] Cobalt(III) dimethylglyoxime complex with two 1-methylimidazoles as the axial ligands.[10b] [b] These protons may be subject to an additional downfield shift due to their proximity to the porphyrin nitrogen atoms (see text).

Poor agreement was also obtained when the close-range approximation for **3a** was used to calculate ring current shifts for the NH and pyridine *ortho* protons in **1** and **1a**, respectively, and it was not possible to fit the ring current shifts of both protons by varying the parameters *b* and *h*. As the NH shift in **1** (−2.0 ppm) is reasonably close to that in **3** (−3.75 ppm),[10b] the parameter *h* was fixed at a standard porphyrin value of 3.80 Å,[10b] and *b* was changed to −0.31 to give the best agreement with the ring current shift for the NH protons. There was then a small discrepancy between the observed (−5.68 ppm) and calculated (−6.21 ppm) ring current shifts for the pyridine *ortho* protons. This may be due to a weak hydrogen bond[24] between the pyridine *ortho* protons and the pyrrole nitrogen atoms which are calculated to be in close proximity [see Fig. 2(*b*) of the preceding paper]. The extra low-field shift of 0.53 ppm is a reasonable value on the basis of this hypothesis, as the low-field shift of the chloroform proton when hydrogen bonded to amines is approximately 1.5 ppm.[25]

Comparisons with previous studies

In a number of earlier investigations, a decrease in the ring current effect in highly substituted porphyrins has been invoked to explain the chemical shift changes relative to less substituted and thus more planar analogues.[13] For example, a reduced ring current effect was suggested to account for the downfield shift of the NH protons in 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5,15-bis(2,5-dimethoxyphenyl)porphyrin ($\delta_{NH} = -1.80$ ppm) compared to the 5-aryl porphyrin ($\delta_{NH} = -2.50$ ppm) and the etio-type porphyrins without *meso* substituents ($\delta_{NH} = -3.75$ ppm).[13a] The downfield shift seen for the NH protons in two series of porphyrins in which the pyrrole hydrogens in **3** are progressively replaced with phenyl substituents (ultimately yielding **6**)[13b] or with ethyl substituents (ultimately yielding **1**)[13c] has also been explained in terms of a decrease in the porphyrin ring current effect as the number of substituents increases and the porphyrin becomes more nonplanar. Finally, chemical shift differences between **7**, which is closely related to **1**, and an analogue without *meso* phenyl substituents have been attributed to a decrease in the porphyrin ring current effect caused by nonplanarity.[13d]

The present study is the first detailed investigation of how extremely large nonplanar distortions affect the ring currents in porphyrins. Important factors considered in our study but not in previous investigations are nonplanarity-induced changes in the positions and orientations of the substituents and the current loops, as well as the ring currents of axial ligands and *meso* phenyl substituents. When these effects are included in the ring current calculations, the ring current in the highly nonplanar porphyrin **1a** is found to be similar to that previously determined for **3a**,[10b,d] and the ring current in another highly nonplanar porphyrin with a different distortion mode, **2a**, is found to be decreased by only 5% compared to **3a**. In contrast to earlier studies,[13] the present study therefore suggests that even extreme nonplanar distortions cause little if any decrease in the porphyrin ring current effect.

In three earlier studies,[13a–c] the only parameter used to measure the porphyrin ring current effect was the chemical shift of the NH protons. The present study shows that this is a poor measure of the porphyrin ring current effect. For example, the chemical shift of the NH protons would lead one to assume a very large decrease in the ring current of **2**. However, the chemical shifts of the pyrrole protons in **2** and the porphyrin and axial ligand protons in complex **2a** indicate that this is not the case. The similarity of the H-10 and H-20 *meso* proton shifts in the etio, 5-aryl and 5,15-diaryl porphyrins (10.15 ± 0.04 ppm)[13a] is also at odds with a downfield shift of approximately 2 ppm for the NH protons. An approximately 2 ppm upfield shift of the methylene protons in porphyrin **7** *versus* a system lacking *meso* substituents is also clearly not due to a decrease in the porphyrin ring current effect.[13d]

It is worth noting that the ring current changes in **1a** and **2a** are quite small compared to those seen when π-electrons are removed from the macrocycle by reduction.[12] For example, the ring currents in chlorins were simulated by eliminating the dipoles for the reduced ring, and decreasing the pyrrole and hexagon dipoles by 10% compared to the corresponding porphyrins.[12b] Modelling the ring currents in isobacteriochlorins, where two adjacent rings are reduced, necessitated the removal of the dipoles for the reduced rings, a decrease of 16% in the pyrrole dipoles and a dramatic 59% reduction in the hexagon dipoles.[12b]

Determination of binding geometries for other ligands

The double-dipole model for nonplanar porphyrins was then used to calculate binding geometries for 1-methylimidazole ligands (complexes **1d** and **2d**) and 4-methylpiperidine ligands (complexes **1f** and **2f**) from their ring current shifts, as described previously for complexes **3d** and **3f**.[10b] The chemical shifts and ring current shifts for complexes **1d**, **2d** and **3d**[10b] are given in Table 2. The binding geometries of the axial ligands in complexes **1d** and **2d** were calculated using the same ligand geometry employed for **3d**,[10b] with the $Co^{III}–N_{ligand}$ distance being varied to obtain the best agreement between the observed and calculated ring current shifts. The ligands in complexes **1d** and **2d** were orientated exactly parallel to the porphyrin cavities, and the H-2 and H-4 protons in **1d** were excluded from the refinement because of their proximity to the porphyrin nitrogen atoms and the possibility of a hydrogen bonding effect.

Excellent agreement between the observed and calculated ring current shifts was then obtained for the remaining protons in complexes **1d** and **2d** (Table 2). In the case of complex **1d**, the $Co^{III}–N_{ligand}$ distance determined from the ring current shifts (1.97 Å) was close to that obtained from the molecular modelling studies (1.935 Å). A similar $Co^{III}–N_{ligand}$ distance (1.93 Å)[10b] was determined from the ring current shifts in **3d**, assuming free rotation of the axial ligands. This also compared favourably with $Co^{III}–N_{ligand}$ distances of 1.906(15) and 1.945(15) Å for the two independent molecules in the crystal structure,[26] and with a distance of 1.959 Å in the calculated minimum energy structure.[17] In the case of **2d**, the ring current studies gave a slightly longer $Co^{III}–N_{ligand}$ distance (2.08 Å) than the molecular modelling studies (1.943 Å).

Table 3 Chemical shifts, ring current shifts and calculated ring current shifts for the liand protons in **1f**, **2f** and **3f**

	Chemical shifts			Ring current shifts					
	1f	**2f**	Ref.[a]	**1f**	Calc.	**2f**	Calc.	**3f**	Calc.
H-2ax	−3.24	−2.80	1.70	−4.94	−4.88	−4.50	−4.52	−5.63	−5.58
H-2eq	−3.06	−3.47	2.77	−5.83	−5.78	−6.24	−6.16	−7.13	−7.01
H-3ax	−1.69	−1.68	0.88	−2.57	−2.61	−2.56	−2.39	−2.86	−2.86
H-3eq	−0.38	−0.34	1.53	−1.91	−2.03	−1.87	−2.14	−2.13	−2.22
H-4ax	−0.65	−0.58	1.35	−2.00	−2.16	−1.93	−2.08	−2.20	−2.25
4-Me	−0.27	−0.17	0.80	−1.07	−1.04	−0.97	−0.96	−1.14	−1.20
Co^{III}–N$_{ligand}$/Å					2.20		2.06		2.05
N$_{porphyrin}$–Co^{III}–N$_{ligand}$ (°)					110		105		105
Co^{III}–N$_{ligand}$–C$_{ligand}$ (°)					112		124		116

[a] Cobalt(III) dimethylglyoxime complex with one 4-methylpiperidine and one chloride anion as the axial ligands.[10b]

An investigation of the 4-methylpiperidine complexes was more complicated because several additional parameters are needed to define the complexation geometry of the ligand.[10b] In a previous study of **3f**,[10b] the geometry of the piperidine ring was fixed, free rotation of the axial ligands was assumed, and the Co^{III}–N$_{ligand}$ distance and the N$_{porphyrin}$–Co^{III}–N$_{ligand}$ and Co^{III}–N$_{ligand}$–C$_{ligand}$ angles were varied to obtain the best agreement between the observed and calculated ring current shifts. A similar approach was used in the present study, except that the plane of the 4-methylpiperidine ligand was fixed parallel to the porphyrin cavity during the ring current calculations. Molecular mechanics calculations indicated that this was the lowest energy orientation of the 4-methylpiperidine ligand in complexes **1f** and **2f**.[17] As in our earlier study,[10b] the NH protons were omitted from the search procedure because they might have been subject to complexation effects that are not fully taken into account by the reference complex.

The ring current calculations again gave good agreement between the observed and calculated ring current shifts (Table 3). The Co^{III}–N$_{ligand}$ distance obtained for **2f** (2.06 Å) was in excellent agreement with that obtained from molecular modelling studies (2.059 Å). A similar Co^{III}–N$_{ligand}$ distance (2.05 Å) was obtained from the ring current shifts of **3f**,[10b] compared to 2.060(3) Å in the crystal structure[27] and 2.046 Å determined from molecular mechanics calculations.[17] In the case of **1f**, the Co^{III}–N$_{ligand}$ distance calculated from the ring current shifts (2.20 Å) was slightly longer than that obtained from the modelling studies (2.027 Å).

Molecular modelling studies have also shown that there is a large (72–88 kJ mol^{-1}) increase in the calculated energies of complexes **1d**, **1f**, **2d** and **2f** when the plane of one ligand is constrained to be at 90° to the porphyrin cavity.[17] The geometry optimization procedure might therefore be expected to give poor solutions when the planes of the axial ligands are fixed perpendicular to the porphyrin cavities during the search procedure. This was indeed found to be the case, with the best solutions having unrealistically long Co^{III}–N$_{ligand}$ distances and poorer agreement factors than when the ligand planes were orientated parallel to the porphyrin cavities.

Experimental

Complex **4a** was prepared from **4**[14a] using the same procedure described for the preparation of **1a** from **1**.[15b] 300 MHz ^{1}H NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 at ambient temperature (296 ± 4 K), and referenced to $SiMe_4$ or the solvent signal at 5.30 ppm ($CHDCl_2$) or 7.26 ppm ($CHCl_3$). The temperature control unit used in the variable temperature NMR experiment of **2** was calibrated using a sample of methanol.[28]

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