Synthesis and unusual properties of the first 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraalkylporphyrin

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The new perhalogenated porphyrin 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraalkylporphyrin (9) (M = Ni), was then isolated in 88% yield after column chromatography (silica gel/cyclohexane) and recrystallization (from CHCl₃ with slow diffusion of MeOH). Porphyrin 9 (M = Ni) gave satisfactory mass spectral analysis (M+ 1269.27: calc. for C₉₅N₂Br₈F₁₂Ni 1269.27) and microanalysis (found C, 23.54; H, 0.00; N, 4.43; calc. C, 23.79; H, 0.00; N, 4.62%).

During the last decade a number of highly nonplanar dodecaalkylporphyrins have been synthesized, including dodecaarylporphyrins (e.g. 1), dodecaalkylporphyrins (e.g. 2), and bromodeaalkylation which occur during the bromination of tetraalkyl- and octaalkyl-porphyrins. Here we report the first synthesis of a tetraalkylcatalalloporphyrin, 9 (M = Ni), and describe some of the unusual features of this compound.

In an attempt to avoid the side-reactions seen during the bromination reactions of tetraalkyl- and octaalkyl-porphyrins, we investigated bromination of the tetra(perfluoroalkyl)porphyrin 10 (M = Ni). The precursor porphyrin 10 (M = 2H) was prepared using a literature procedure. Refluxing 10 (M = 2H) with Ni(acac)₂ in toluene gave 10 (M = Ni) which was more suitable for use in the bromination reactions. Bromination of 10 (M = Ni) proved difficult but was eventually achieved by refluxing a solution of the porphyrin in CHCl₃ containing a large excess of Br₂ for 10 days under argon. The perhalogenated porphyrin 9 (M = Ni) was then isolated in 88% yield after column chromatography (silica gel/cyclohexane) and recrystallization (from CH₂Cl₂ with slow diffusion of MeOH).

Porphyrin 9 (M = Ni) gave satisfactory mass spectral analysis (M+ 1269.27; calc. for C₉₅N₂Br₈F₁₂Ni 1269.27) and microanalysis (found C, 23.54; H, 0.00; N, 4.43; calc. C, 23.79; H, 0.00; N, 4.62%), and was further characterized by X-ray crystallography and visible and NMR spectroscopy as described below.

The crystal structure of 9 (M = Ni)† (Fig. 1) revealed a very ruffled macrocycle in which the meso positions were displaced alternately up or down by an average of 1.06 Å with respect to the least-squares plane of the porphyrin ring. The average out-of-plane displacement for all of the porphyrin atoms with respect to the least-squares plane of the porphyrin macrocycle was 0.50 Å. By these measures 9 (M = Ni) is the most ruffled porphyrin ever reported; the largest ruffling distortion previously observed was for 11 (M = Zn), where the corresponding displacements were only 0.90 and 0.44 Å. The conformation seen for 9 (M = Ni) can be contrasted with the saddle conformation seen for the perhalogenated tetraarylporphyrin 12 (M = Ni), where the meso carbons are in the least-squares plane of the porphyrin macrocycle and the pyrrole rings are tilted alternately up or down. The strongly ruffled structure of 9 (M = Ni) is accompanied by an extremely short Ni–N distance of only 1.88 Å. This can be compared to Ni–N distances of 1.90 Å in the very saddle-distorted porphyrin 12 (M = Ni)² and 1.96 Å in planar (triclinic A) NiOEP. The significant shortening of the Ni–N distance seen for 9 (M = Ni) is consistent with the
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larger degree of core contraction expected for ruffling versus other types of nonplanar distortion. Molecular modelling studies using a previously published force-field demonstrated that the conformations seen in the crystal structures of 9 (M = Ni) and 12 (M = Ni) were the minimum energy structures for these porphyrins, and that the different Ni-N distances in the two compounds could be accurately reproduced.

Porphyrin 9 (M = Ni) possesses some unusual spectroscopic characteristics. Nonplanarity is known to cause a red-shift in the optical spectra of porphyrins due to a greater destabilization of the HOMO compared with the LUMO, and the optical characteristics. Nonplanarity is known to cause a red-shift in the band upon addition of eight bromo substituents to the macrocycle. The barrier for rotation of the CF3 groups in the ruffled structure and hindered CF3 rotation is a rare phenomenon but has been observed in some very sterically crowded compounds. For example, the activation energy for CF3 rotation in CF3CCl2 is unusually slow rotation of the CF3 groups in 9 (M = Ni) gave a single sharp CF3 signal at all of the temperatures studied. The non-equivalence of the trifluoromethyl fluorines in 9 (M = Ni) indicates that rotation of the CF3 groups is slow on the NMR timescale at low temperatures. Hindered CF3 rotation is a rare phenomenon but has been observed in some very sterically crowded compounds. For example, the activation energy for CF3 rotation in CF3CCl2 is 36 kJ mol$^{-1}$ at 201 K, with the coupling constant between the fluorines being 101 Hz in the slow exchange spectrum. The unusually slow rotation of the CF3 groups in 9 (M = Ni) provides evidence of a very high degree of steric crowding in this compound.

In earlier NMR studies of nonplanar porphyrins, dynamic processes in $M = 4H$, 1,2 (M = Ni)$^{14}$ and 15 (M = 2H or Zn)$^{15}$ were initially attributed to macrocyclic inversion but subsequently reassigned as substrate rotation.$^{16-18}$ In an attempt to avoid any confusion about the nature of the dynamic process in 9 (M = Ni), we used molecular mechanics calculations$^{8,9}$ to estimate the energies of the two possible CF3 rotation pathways (CF3 rotation about a ruffled porphyrin core versus CF3 rotation during inversion of the porphyrin macrocycle). The barrier for rotation of the CF3 groups in the ruffled structure was calculated to be 34 kJ mol$^{-1}$. The lowest energy inversion–rotation barrier (103 kJ mol$^{-1}$) was found between the ruffled structure (designated o-CF3) and a structure which had three CF3 groups on the same side of the porphyrin plane (designated a-CF3). On the basis of these calculated energies it seems probable that the process being observed for 9 (M = Ni) is rotation of the CF3 groups in the ruffled structure.

Porphyrin 9, with a novel combination of a strongly ruffled macrocycle and very electron-withdrawing substituents, clearly has many unusual features even when compared with other very nonplanar dodecasubstituted porphyrins. It will be interesting to investigate this porphyrin further and perhaps to examine how 9 compares with tetraethyltahalaporphyrins in terms of catalyzing the oxygenation reactions of unactivated alkanes.$^{19}$

Notes and references

† Crystals were grown by the slow diffusion of cyclohexane into a CH2Cl2 solution of 9 (M = Ni) (C24H24Br2P4Zn2Ni). The selected crystal (0.05 x 0.06 x 0.04 mm) had an orthorhombic unit cell, space group Pnma, cell dimensions $a = 8.110(6)$, $b = 23.587(2)$, $c = 15.583(14)$ Å, $V = 2981.2(5)$ Å$^3$, $Z = 4$ (FW = 1270.27). Data were collected in $\omega$ scan mode to $\theta_{\text{max}} = 63^\circ$ (29685 total reflections measured) on a Bruker SMART 1000 diffractometer with graphite monochromated radiation from a ceramic sealed tube source ($\lambda(\text{Mo-K\alpha}) = 0.71073$ Å). The crystal was cooled to 93(2) K during data collection with an anhydrous N2 stream supplied from a linear flow cryostat. The slow temperature separation. The structure was solved by direct methods (SHELXS-97) and refined (based on $F^2$ using all data) by full matrix least-squares methods with 232 parameters (SHELXL-97). Of 3511 unique reflections used in the refinement ($2\theta_{\text{max}} = 55^\circ$, 1937 were observed ($I > 2\sigma(I)$). An empirical absorption correction (SADABS) (ref. 20) was applied ($T_{\text{min}} = 0.546$, $T_{\text{max}} = 0.657$, $\rho_{\text{calc}} = 2.83$ g cm$^{-3}$, $\mu = 11.47$ mm$^{-1}$). Final $R$ factors were $R1 = 0.042$ (observed data) and $wR2 = 0.077$ (all data), CCDC 162/1413.

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