SAND99-1254J

Correspondence to: Dr. Craig J. Medforth
Department of Chemistry
University of California
Davis, California 95616
U.S.A.

Phone: (530) 752-8308
FAX: (530) 752-8995
email: medforth@indigo.ucdavis.edu

Draft of
May 5th, 1999

Synthesis and characterization of a new perhalogenated porphyrin

Nora Y. Nelson,[1] Craig J. Medforth,[1,*] Daniel J. Nurco, Songling Jia,[2] John Shelnutt[2] and Kevin M. Smith[1,*]

[1]*Department of Chemistry, University of California, Davis, California 95616, U.S.A.*
[2]*New Materials Theory and Validation Department, Sandia National Laboratories, Albuquerque, New Mexico 87185-1349, U.S.A.*

The first synthesis of an octahalotetraalkylporphyrin [2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(trifluoromethyl)porphinato nickel(II)] is reported; this perhalogenated porphyrin has several novel properties including a very nonplanar ruffled structure with an unusually short Ni-N distance, an extremely red-shifted optical spectrum, and hindered rotation of the trifluoromethyl groups ($\Delta G^{\ddagger}_{278K} = 47$ kJ mol^{-1}).

A range of dodecasubstituted porphyrins have been synthesized during the last decade with the aim of investigating the effects of nonplanar distortions on the properties of porphyrins.[1]

Examples include dodecaarylporphyrins (e.g. **1**), dodecaalkylporphyrins (e.g. **2**), octaalkyltetraphenylporphyrins (e.g. **3**), octahalotetraarylporphyrins (e.g. **4**), octaethyltetranitroporphyrin (**5**), and systems with substituents fused to the pyrrole rings (e.g. **6** and **7**). Detailed studies of these porphyrins have served to increase speculation about a possible functional role for the nonplanar deformations seen for some tetrapyrroles in biological systems.[1] Two classes of dodecasubstituted porphyrin which have so far proved elusive are the octahalotetraalkylporphyrins (**8**) and octaalkyltetrahaloporphyrins (**9**); the unavailability of these compounds can be related to undesirable side-reactions which occur during the bromination of tetraalkyl- and octaalkyl-porphyrins.[2] In this paper we report the first successful synthesis of an octahalotetraalkylporphyrin (**10**, M = Ni) and describe some of the unusual structural and spectroscopic properties of this porphyrin.

In an attempt to avoid the side-reactions seen during the brominations of tetraalkyl- and octaalkyl-porphyrins, we investigated bromination of the more inert tetra(perfluoroalkyl)porphyrin **11** (M = Ni). The precursor porphyrin **11** (M = 2H) was prepared using a literature procedure.[3] Refluxing **11** (M = 2H) with Ni(acac)$_2$ in toluene then gave **11** (M = Ni) which was more suitable for use in bromination reactions. Bromination of **11** (M = Ni) proved quite difficult but was eventually achieved using a very large excess of Br$_2$ in refluxing chloroform under argon for ten days. The perhalogenated porphyrin **10** (M = Ni) was isolated in 88.4 % yield after column chromatography (silica gel/cyclohexane) and recrystallization (from dichloromethane by slow diffusion of methanol).

As expected for a such a sterically crowded porphyrin, the crystal structure of **10** (M = Ni)[†] shows a very nonplanar conformation (Figure 1). The macrocycle adopts a ruffle conformation in which the meso positions and their substituents are moved alternately up or down with respect to the least-squares plane of the porphyrin macrocycle. Ruffle deformations have also been seen in the crystal structures of other nonplanar porphyrins with meso alkyl substituents e.g. **2** (M = Ni),[4] **12** (M = Zn),[5] and **12** (M = 2H).[6]. In contrast, octabromotetraarylporphyrins display a different structure, the saddle conformation, where the meso carbons are in the least-squares plane of the porphyrin macrocycle and the pyrrole rings are tilted alternately up and down.[7] The average Ni-N distance of 1.87 Å in **10** (M = Ni) is also extremely short, even when compared to other very nonplanar porphyrins such as **13** (M = Ni) where the Ni-N distance is 1.90 Å.[7] The short Ni-N distance in **10** (M = Ni) is consistent with the very high degree of core contraction that has been calculated to occur for ruffling versus other types of distortion.[8]

Porphyrin **10** (M = Ni) has some interesting spectroscopic characteristics. Nonplanarity of the porphyrin macrocycle is known to cause a red-shift in the optical spectra of porphyrins due to a greater destabilization of the HOMO than of the LUMO.[1] The red-shifts of the $Q_{(0,0)}$ band upon addition of eight β bromine substituents to **14** (M = Ni) and **15** (M = Ni) are 1050 and 1250 cm^{-1}, respectively. However, the red-shift of the $Q_{(0,0)}$ band upon addition of eight β bromine substituents to **11** (M = Ni) is substantially larger (2450 cm^{-1}). We suspect that the increased red-shift in **10** (M = Ni) is a result of the ruffled conformation adopted by this porphyrin, as other properties of the porphyrin π-system (e.g. the frequencies of Raman marker line and the ring current effect[9]) also appear to be affected more by ruffle distortion than by saddle distortion.

The ^{19}F NMR spectrum of **10** (M = Ni) in CD_2Cl_2 at ambient temperature (Figure 2) displays an extremely broad signal at δ -39 (referenced to internal $CFCl_3$ at δ -8.0)[10] for the trifluoromethyl groups. A sharp singlet at δ -39.0 is observed upon heating the complex, whereas cooling causes the broad peak to split into two signals at δ -34.7 (d, 2F, J_{F-F} = 114 Hz) and δ -47.81 (t, 1F, J_{F-F} = 114 Hz). The activation ($\Delta G^{\ddagger}$) for the observed dynamic process, calculated at the coalescence temperature of 278 K, is 47 kJ mol^{-1}. The non-equivalence of the trifluoromethyl fluorines at low-temperatures indicates that rotation of the CF_3 groups is slow on the NMR timescale. Hindered CF_3 rotation is rare but has previously been observed in very sterically crowded compounds. For example, the activation energy for CF_3 rotation in CF_3Cl_2I is 36 kJ mol^{-1} at 201 K.[11] In this case, the coupling constant between the fluorines (101 Hz) is similar to that observed for **10** (M = Ni). The unusually slow rotation of the CF_3 groups in **10** (M = Ni) thus indicates a very high degree of steric crowding for the CF_3 groups even though they are moved away from the bromine substituents by the ruffling distortion of the porphyrin ring. Not surprisingly, CF_3 rotation is fast on the NMR timescale at all temperatures studied for the unbrominated precursor **11** (M = Ni) where severe steric crowding of the peripheral substituents is not present.

Interestingly, it is not clear if the activation energy obtained from NMR studies of **10** (M = Ni) actually represents the barrier for rotation of the trifluoromethyl groups. An alternative process, macrocyclic inversion with concurrent CF_3 rotation, could also provide the observed averaging of the trifluoromethyl fluorines. Indeed, in earlier studies of nonplanar porphyrins the alkyl rotation processes in **2** (M = Ni)[4] and **16** (M = 2H or Zn)[12] and the β aryl rotation process in **1** (M = 4H)[4] were mistakenly assigned as macrocyclic inversion.[13-15] For the present work, we tried for the first time to differentiate rotation and inversion processes in nonplanar porphyrins by calculating the energy barriers for these processes using a molecular mechanics force field optimized for porphyrins.[16]

The global minimum energy structure calculated for **10** (M = Ni) using our force field was found to agree very well with the crystal structure shown in Figure 1. The lowest energy inversion pathway found was found to be one in which CF_3 groups were forced sequentially through the porphyrin plane i.e. αβαβ (crystal structure) -> αααβ -> αααα -> βααα > βαβα (inverted crystal structure). Both the αααβ and αααα intermediate structures were found to be stable local minima ($\Delta E = 43$ kJ mol^{-1} and 81 kJ mol^{-1}). The highest barrier along this pathway was between the αααβ and αααα structures ($\Delta E = 147$ kJ mol^{-1}), although rotation of the CF_3 groups also occurred at a considerably lower barrier ($\Delta E = 103$ kJ mol^{-1}) during interconversion between the αβαβ and αααβ structures. The barrier for rotation of the trifluoromethyl group in the ruffled (αβαβ) structure was calculated to be 34 kJ mol^{-1}. The observed activation energy (47 kJ mol^{-1}) is quite close to the calculated CF_3 rotation barrier (34 kJ mol^{-1}) but much less than the calculated inversion/rotation barrier (103 kJ mol^{-1}). This strongly suggests that the observed dynamic process is trifluoromethyl rotation about the same ruffled conformation seen in the crystal structure, and also lends support to the idea of using molecular mechanics calculations to differentiate dynamic processes in porphyrins.

Porphyrin **10** is clearly unusual even when compared to other very nonplanar dodecasubstituted porphyrins. It will be interesting to see if the previously unavailable combination of very electron withdrawing substituents on a strongly ruffled porphyrin core results in additional anomalous behaviour. It will also be interesting to examine how metal complexes of **10** compare to metal complexes of octahalotetraarylporphyrins in terms of their ability to catalyze the oxygenation reactions of unactivated alkanes.[17]

This work was supported by grants from the National Institutes of Health (HL 22252) and the National Science Foundation (CHE-96-23117). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed-Martin company, for the United States Department of Energy under Contract DE-ACO4-94AL85000.

References:

1. J. A. Shelnutt, X.-Z. Song, J.-G. Ma, S.-L. Jai, W. Jentzen and C. J. Medforth, *Chem. Soc. Rev.*, 1998, **27**, 31 and references cited.

2. N. Y. Nelson, C. J. Medforth, R. G. Khoury, D. J. Nurco and K. M. Smith, *Chem. Commun.*, 1998, 1687 and references cited.

3. S. G. DiMagno and R. A. Williams, *J. Org. Chem.*, 1994, **59**, 6943.

4. C. J. Medforth, M. O. Senge, K. M. Smith, L. D. Sparks and J. A. Shelnutt, *J. Am. Chem. Soc.*, 1992, **114**, 9859.

5. M. O. Senge, T. Ema and K. M. Smith, *J. Chem. Soc., Chem. Comm.*, 1995, 733.

6. M. S. Somma, C. J. Medforth, N. Y. Nelson, M. M. Olmstead, R. G. Khoury and K. M. Smith, *Chem. Commun.*, 1999, in press

7. D. Mandon, P. Ochsenbein, J. Fischer, R. Weiss, K. Jayaraj, R. N. Austin, A. Gold, P. S. White, O. Brigaud, P. Battioni and D. Mansuy, *Inorg. Chem.*, 1992, **31**, 2044.

8. X. Z. Song, L. Jaquinod, W. Jentzen, D. J. Nurco, S. L. Jia, R. G. Khoury, J. G. Ma, C. J. Medforth, K. M. Smith and J. A. Shelnutt, *Inorg. Chem.*, 1998, **37**, 2009.

9. C. J. Medforth, C. M. Muzzi, K. M. Shea, K. M. Smith, R. J. Abraham, S. Jia and J. A. Shelnutt, *J. Chem. Soc., Perkin Trans. 2*, 1997, 839.

10. R. K. Harris and B. E. Mann, *NMR and the Periodic Table*, Academic Press, 1978.

11. F. J. Weigert and W. Mahler, *J. Am. Chem. Soc.*, 1972, **94**, 5314.

12. K. Maruyama, T. Nagata and A. Osuka, *J. Phys. Org. Chem.*, 1988, **1**, 63.

13. C. J. Medforth, M. O. Senge, T. P. Forsyth, J. D. Hobbs, J. A. Shelnutt and K. M. Smith, *Inorg. Chem.*, 1994, **33**, 3865.

14. M. O. Senge, C. J. Medforth, T. P. Forsyth, D. A. Lee, M. M. Olmstead, W. Jentzen, R. K. Pandey, J. A. Shelnutt and K. M. Smith, *Inorg. Chem.*, 1997, **36**, 1149.

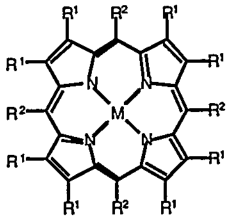
15. C. M. Muzzi, C. J. Medforth, L. Voss, M. Cancilla, C. Lebrilla, J.-G. Ma, J. A. Shelnutt and K. M. Smith, submitted for publication

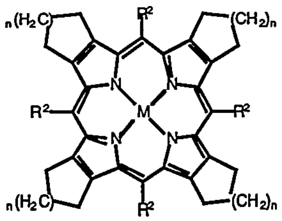
16. J. A. Shelnutt, C. J. Medforth, M. D. Berber, K. M. Bardigia and K. M. Smith, *J. Am. Chem. Soc.*, 1991, **113**, 4077.

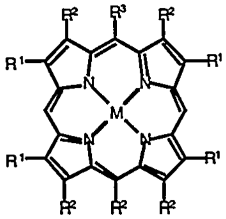
17. J. E. Lyons, P. E. Ellis and H. K. Myers, *J. of Catalysis*, 1995, **155**, 59.

Footnotes:

[†] Crystals of **10**(M = Ni) ($C_{40}H_{54}N_4$) were grown by the slow diffusion of methanol into a solution of **10** (M = Ni) in methanol.







1 $R^1 = R^2 = C_6H_5$

3 $R^1 = CH_2CH_3$; $R^2 = C_6H_5$

4 $R^1 = Br$; $R^2 = C_6H_5$

5 $R^1 = CH_2CH_3$; $R^2 = NO_2$

8 R^1 = Halogen; R^2 = Alkyl

9 R^1 = Alkyl; R^2 = Halogen

10 $R^1 = Br$; $R^2 = CF_3$

11 $R^1 = H$; $R^2 = CF_3$

12 $R^1 = H$; $R^2 = C(CH_3)_3$

13 $R^1 = Br$; $R^2 = C_6F_5$

14 $R^1 = H$; $R^2 = C_6H_5$

15 $R^1 = H$; $R^2 = C_6F_5$

2 $R^2 = (CH_2)_4CH_3$; $n = 1$

6 $R^2 = C_6H_5$; $n = 1$-3

16 R^1 = Methyl; R^2 = Ethyl; R^3 = Alkyl

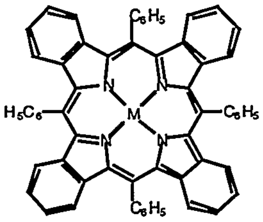


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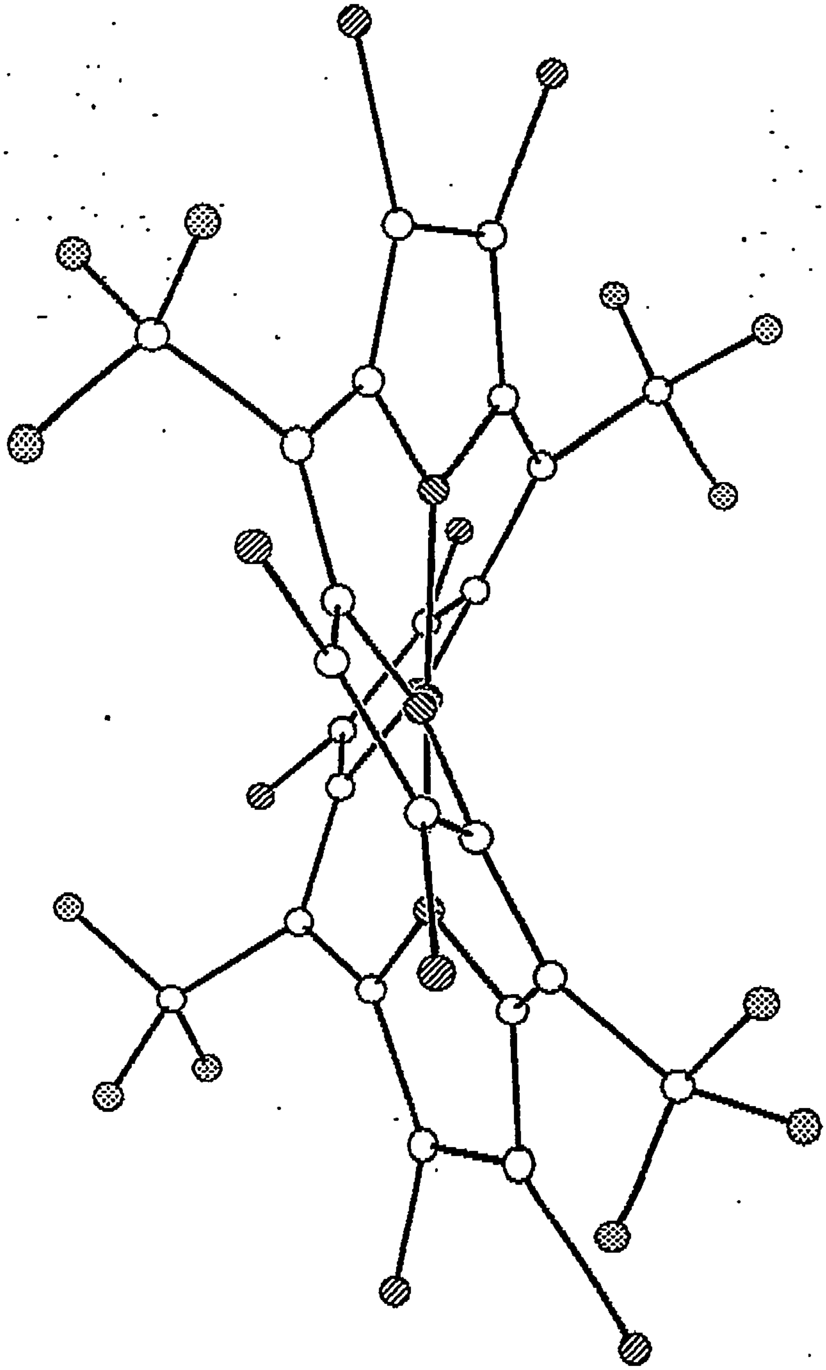
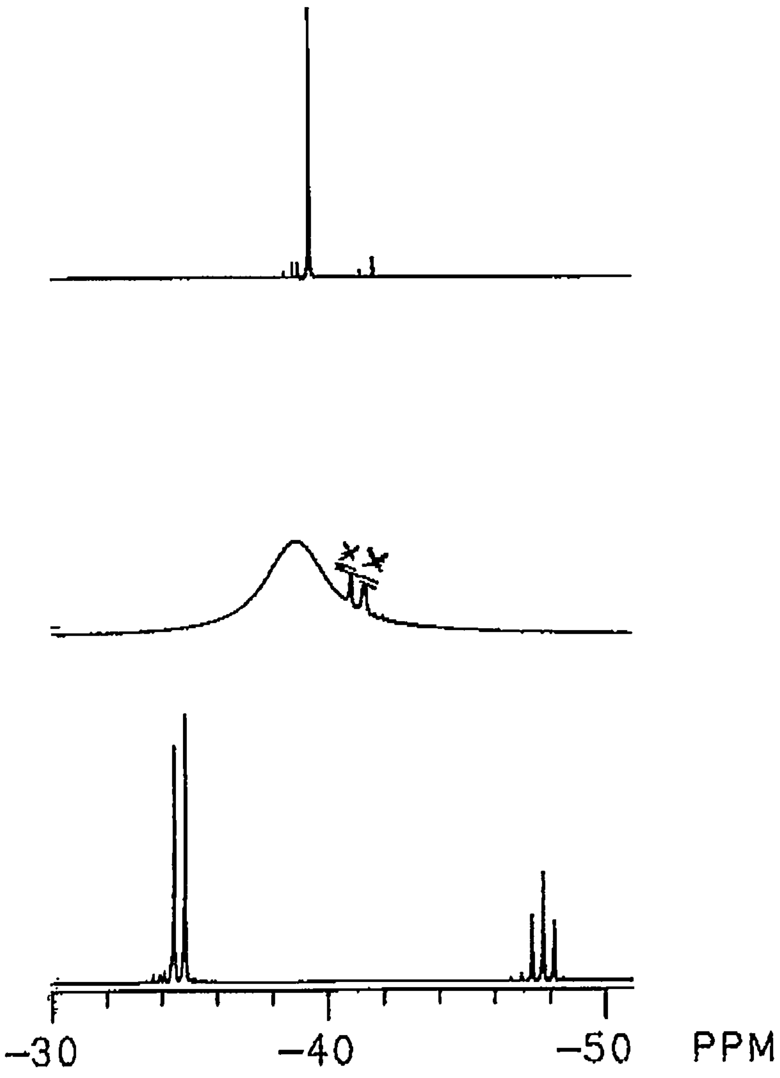
Figure Captions

Figure 1 Crystal structure of porphyrin **10** (M = Ni).

Figure 2 ^{19}F NMR spectra of **10** (M = Ni) in $CDCl_2CDCl_2$ at 413 K (upper), in CD_2Cl_2 at 293 K (middle), and in CD_2Cl_2 at 193 K (lower). Peaks marked 'x' correspond to truncated signals from small amounts of impurites.




×
×
−30
−40
−50
PPM