Phosphorus octaethyltetraphenylporphyrins [(oetpp)P(Me)(X)]PF_6 (X = Me, OH, F) having saddle (X = Me) or ruffled (X = OH, F) conformations

Akihiro Yamamoto, Wataru Satoh, Yohsuke Yamamoto* and Kin-ya Akiba*

Department of Chemistry, Faculty of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan. E-mail: akiba@sci.hiroshima-u.ac.jp

Received (in Cambridge, UK) 5th October 1998, Accepted 8th December 1998

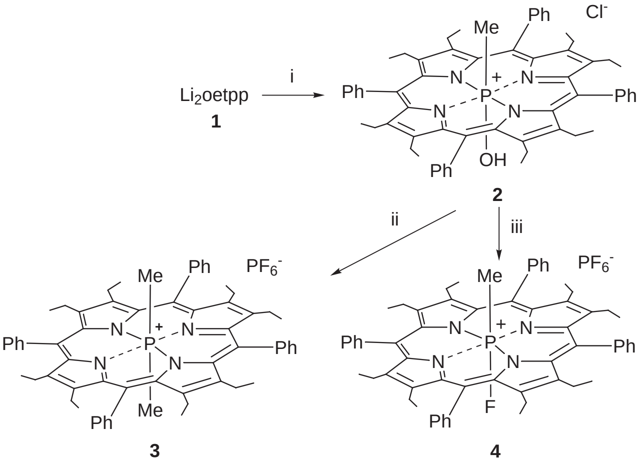
X-Ray crystallographic structures of [(oetpp)P(Me)(X)]PF_6 revealed that the axial ligand (X) plays a major role in changing the conformation of the porphyrin core from saddle (X = Me) to ruffled (X = OH and F).

There has been considerable interest in the conformations of metalloporphyrins since they have a profound influence on the physicochemical properties of the macrocycle such as redox potential and electron transfer rates, and therefore its reactivity in a protein.[1] The interest has prompted the synthesis of many substituted porphyrins in which deformations (mainly saddle type deformation) from planarity are induced by crowding of substituents at the periphery of the macrocycle.[2] There is now a considerable body of information describing the structural and spectroscopic properties of highly non-planar octaalkyltetraphenylporphyrins bearing transition metals[3] which show saddle conformations. Although those bearing main group elements have not been reported, phosphorus octaalkyltetraphenylporphyrins are interesting because phosphorus has been the smallest atom which can occupy the center of a porphyrin ring. Recent report on X-ray crystallographic structures of $[(oep)P(X)(Y)]^+Z^-$ revealed essentially ruffled conformations in order to accommodate the small phosphorus atom. The electronegativities of the axial ligands (X and Y) played a major role in determining the deformation, for example, $[(oep)P(Me)_2]PF_6$ showed a planar conformation.[4] Here we report the synthesis and X-ray structures of phosphorus octaethyltetraphenylporphyrins, [(oetpp)P(Me)(X)]PF_6 (X = OH **2**, Me **3**, F **4**), which showed strong effects of the axial ligands on the conformations, *i.e.*, a saddle conformation was observed in $[(oetpp)P(Me)_2]PF_6$ (**3**-PF_6) but ruffled ones were observed in [(oetpp)P(Me)(OH)]ClO_4 (**2**-ClO_4) and [(oetpp)P(Me)(F)]PF_6 (**4**-PF_6).

The reaction of oetppLi$_2$ **1** with $MePCl_2$ was carried out under dichloromethane reflux for 12 h. After removal of the solvent and excess of $MePCl_2$, the residue was subjected to neutral alumina column chromatography (CH_2Cl_2) to give [(oetpp)P(Me)(OH)]Cl (**2**-Cl) (Scheme 1). After counter anion exchange **2**-ClO_4 was obtained pure for elemental analysis.

The hydroxy group of **2**-Cl was substituted by a methyl group by the reaction of **2**-Cl with phosphorus trichloride followed by treatment with an excess of trimethylaluminium in dichloromethane to yield $[(oetpp)P(Me)_2]PF_6$ (**3**-PF_6) in 79% yield after counter anion exchange according to the method recently reported by us for group 15 element porphyrins.[5] [(oetpp)P(Me)(F)]PF_6 (**4**-PF_6) was obtained in 61 % yield by the reaction of **2**-PF_6 with phosphorus trichloride (Scheme 1).[6]

Crystals of **2**-ClO_4, **3**-PF_6 and **4**-PF_6 suitable for X-ray analysis were grown from dichloromethane–*n*-hexane. The crystallographic analyses of **3**-PF_6 and **4**-PF_6 are not of good quality owing to extensive disorder of the counter anion (PF_6^-) and dichloromethane as a solvent in **4**-PF_6, but the structures of the porphyrin core could be definitely determined. Figs. 1–3 show ORTEP drawings of **2**-ClO_4, **3**-PF_6 and **4**-PF_6 (counter anions and dichloromethane in **4**-PF_6 are omitted for clarity). The crystal structure of **3**-PF_6 exhibits a distorted saddle conformation which is characterized by large displacements of $C_{pyrrole\text{-}\beta}$ atoms from the mean plane of the core. By contrast, the crystal structures of **2**-ClO_4 and **4**-PF_6 exhibit ruffled conformations which are characterized by significant C_{meso} displacements from the core and twist of the pyrrole rings so that the β carbons lie above and below the core plane. **4**-PF_6 is more distorted than **2**-ClO_4 as is evident from the average displacement of the C_{meso} atoms from the mean plane of the molecule (**4**-PF_6, 1.20 Å; **2**-ClO_4, 1.07 Å).



Scheme 1 *Reagents and conditions*: i, $MePCl_2$, CH_2Cl_2, reflux, 12 h; ii, PCl_3, CH_2Cl_2, reflux, 3 h, then $AlMe_3$ in hexane, CH_2Cl_2, room temp., 12 h; iii, KPF_6; then PCl_3, CH_2Cl_2, room temp., 12 h.

The results can be explained based on the conclusions found for [(oep)P(X)(Y)]Z.[4] The introduction of the electronegative axial substituents [X = OH **2** and X = F **4** in (oetpp)P(Me)(X)] reduces the size of the central phosphorus atom and the average P–N bond distances become shorter [1.94(1) Å in **3**-PF_6 (X = Me), 1.849(4) Å in **2**-ClO_4 (X = OH) and 1.810(8) Å in **4**-PF_6 (X = F)], and leads to the ruffled conformation becoming preferable in **2**-ClO_4 and **4**-PF_6 in order to accommodate the

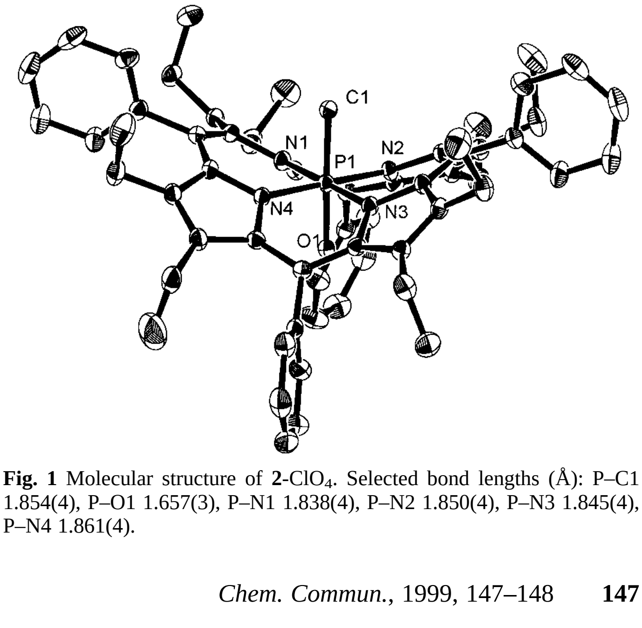


Fig. 1 Molecular structure of **2**-ClO_4. Selected bond lengths (Å): P–C1 1.854(4), P–O1 1.657(3), P–N1 1.838(4), P–N2 1.850(4), P–N3 1.845(4), P–N4 1.861(4).

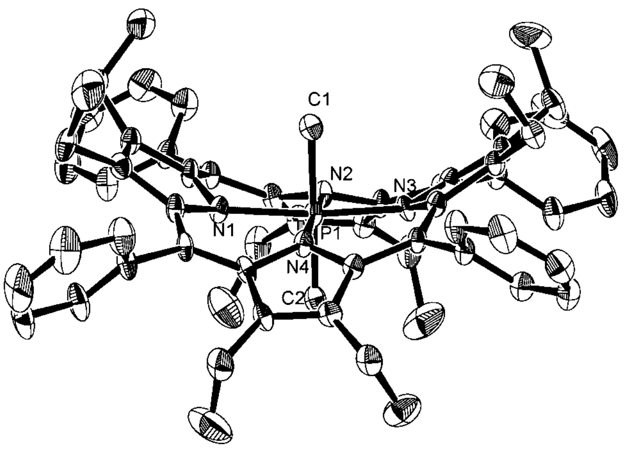


Fig. 2 Molecular structure of **3**-PF$_6$. Selected bond lengths (Å): P–C1 1.85(1), P–C2 1.82(1), P–N1 1.949(9), P–N2 1.94(1), P–N3 1.918(9), P–N4 1.95(1).

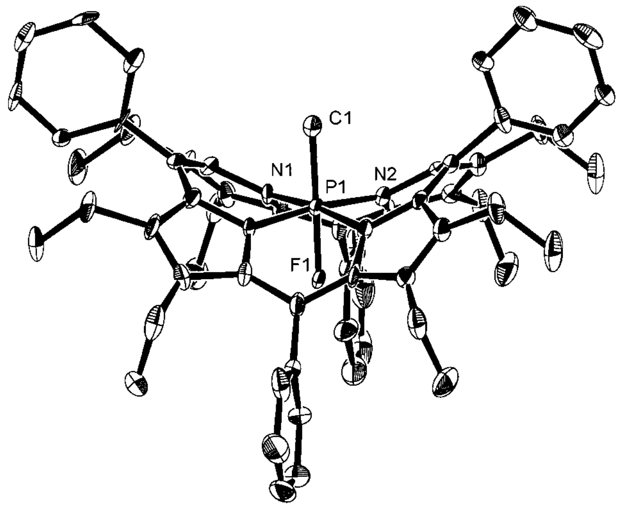


Fig. 3 Molecular structure of **4**-PF$_6$. Selected bond lengths (Å): P–C1 1.83(2), P–F 1.648(9), P–N1 1.827(8), P–N2 1.793(8).

smaller phosphorus atom. Although metal size dependence of the degree of deformation of saddle conformations has already been investigated for transition metals,[3] such large electronic effects of the axial ligands to change the fundamental conformations have never been observed. The structures of **2**-ClO$_4$ and **4**-PF$_6$ are the first examples for metallooctaalkyltetraphenylporphyrins showng ruffled conformations.

It is interesting that the Q(0,0) band of ruffled **2** (627 nm) and **4** (622 nm) are siginificantly blue shifted in the UV–VIS in comparison with that of **3** (667 nm) and free base octaethyltetraphenylporphyrin (686 nm) with saddle conformation.[2] Since such a large shift has not been observed in the [(oep)P(Me)(Y)]Z series, the shift can be ascribed to the difference of core conformations. In order to rationalize the results further structural and spectroscopic studies are now in progress.

Notes and references

† Compounds, **2**-ClO$_4$, **3**-PF$_6$ and **4**-PF$_6$ gave satisfactory C, H, N elemental analyses. *Spectroscopic data*: **2**-ClO$_4$; ^{1}H NMR (CDCl$_3$) δ −4.48 (d, 3H, *J* 14 Hz), 0.85 (t, 24H, *J* 7 Hz), 2.9–3.0 (br m, 16H), 7.48 (t, 8H, *J* 7 Hz), 7.58 (t, 4H, *J* 7 Hz), 7.68 (d, 8H, *J* 7 Hz). ^{31}P NMR (CDCl$_3$) δ −206.4. UV–VIS (CH$_2$Cl$_2$) λ_{max} (log ε) 375 (3.48), 447 (5.34), 579 (3.93), 627(3.49). **3**-PF$_6$; ^{1}H NMR (CDCl$_3$) δ −5.05 (d, 6 H, *J* 16 Hz), 0.64 (t, 24 H, *J* 7 Hz), 2.73 (q, 16 H, *J* 7 Hz), 7.69 (t, 8 H, *J* 7 Hz), 7.77 (t, 4 H, *J* 7 Hz), 8.01 (d, 8 H, *J* 7 Hz). ^{31}P NMR (CDCl$_3$) δ −195.3 (s), −143.9 (spt, *J* 715 Hz). UV–VIS (CH$_2$Cl$_2$) λ_{max} (log ε) 391 (4.87), 467 (5.49), 596 (4.06), 667(4.34). **4**-PF$_6$; ^{1}H NMR (CDCl$_3$) δ −4.14 (d, 3 H, *J* 12 Hz), 0.85 (t, 24 H, *J* 7 Hz), 2.7–3.3 (br m, 16 H), 7.54 (t, 8 H, *J* 7 Hz), 7.6–7.7 (br t, 4 H), 7.62 (d, 8 H, *J* 7 Hz). ^{31}P NMR (CDCl$_3$) δ −203.1 (d, *J* 730 Hz), −143.8 (spt, *J* 715 Hz). UV–VIS (CH$_2$Cl$_2$) λ_{max} (log ε) 443 (5.37), 481 (3.96), 575 (4.13), 622 (3.83).

‡ *Crystal data*: **2**-ClO$_4$·CH$_2$Cl$_2$: C$_{62}$H$_{66}$N$_4$O$_5$Cl$_3$P, M = 1084.5, orthorhombic, space group $P2_12_12_1$, a = 17.30(1), b = 20.64(3), c = 15.196(6) Å, U = 5426(6) Å^3, Z = 4, D_c = 1.22 g cm^{-3}, T = 297 K.

4-PF$_6$·CH$_2$Cl$_2$: C$_{61}$H$_{63}$N$_4$F$_7$Cl$_2$P$_2$, M = 1118.0, monoclinic, space group $P2_1/m$, a = 11.560(2), b = 25.797(5), c = 11.533(2) Å, β = 107.01(1)deg, U = 3288.8(9) Å^3, Z = 2, D_c = 1.13 g cm^{-3}, T = 297 K.

Both data sets were collected on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Unit cell parameters were determined by autoindexing several images in each data set separately with program DENZO.[7] For each data set, rotation images were collected in 6° increments with a total rotation of 180° about ϕ. Data were processed by using SCALEPACK.[7] The structure was solved using the teXsan (Rigaku) system and refined by full-matrix least squares. Final $R1$ = 0.052 (R_w = 0.048) for 5580 observed reflections (676 parameters) with $I > 3\sigma(I)$ in **2**-ClO$_4$·CH$_2$Cl$_2$, and $R1$ = 0.134 (R_w = 0.150) for 2530 observed reflections (392 parameters) with $I > 4\sigma(I)$ in **4**-PF$_6$·CH$_2$Cl$_2$.

3-PF$_6$: C$_{63}$H$_{68}$N$_4$F$_6$Cl$_2$P$_2$, M = 1128.1, triclinic, space group $P\bar{1}$, a = 13.303(3), b = 13.911(5), c = 17.602(3) Å, α = 73.49(2), β = 69.76(1), γ = 71.46(2)°, U = 2841(1) Å^3, Z = 2, D_c = 1.32 g cm^{-3}, T = 297 K. Crystal data for the product were collected on a Mac Science MXC-3 diffractometer and irradiated with graphite-monochromated Cu-Kα radiation (λ = 1.5418 Å). The structure was solved using the teXsan (Rigaku) system and refined by full-matrix least squares. Final $R1$ = 0.105 (R_w = 0.122) for 4308 observed reflections (663 parameters) with $I > 5\sigma(I)$. CCDC 182/1107. See http://www.rsc.org/suppdata/cc/1999/147/ for crystallographgic files in .cif format.

1 For reviews: M. O. Senge, *J. Photochem. Photobiol. B: Biol.*, 1992, **16**, 3; W. R. Scheidt and C. A. Reed, *Chem. Rev.*, 1981, **81**, 543; M. Ravikanth and T. K. Chandrashekar, *Struct. Bonding (Berlin)*, 1995, **82**, 105.

2 For recent reports: K. M. Barkigia, M. D. Berber, J. Fajer, C. J. Medforth, M. W. Renner and K. M. Smith, *J. Am. Chem. Soc.*, 1990, **112**, 8851; S. A. Sibilia, S. Hu, C. Piffat, D. Malamed and T. G. Spiro, *Inorg. Chem.*, 1997, **36**, 1013; K. M. Kadish, E. Van Caemelbecke, F. D'Souza, C. J. Medforth, K. M. Smith, A. Tabard and R. Guilard, *Inorg. Chem.*, 1995, **34**, 2984.

3 L. D. Sparks, C. J. Medforth, M.-S. Park, J. R. Chamberlain, M. R. Ondrias, M. O. Senge, K. M. Smith and J. A. Shelnutt, *J. Am. Chem. Soc.*, 1993, **115**, 581; K. M. Barkigia, M. W. Renner, L. R. Furenlid, C. J. Medforth, K. M. Smith and J. Fajer, *J. Am. Chem. Soc.*, 1993, **115**, 3627.

4 Y. Yamamoto, R. Nadano, M. Itagaki and K.-y. Akiba, *J. Am. Chem. Soc.*, 1995, **117**, 8287.

5 K.-y. Akiba, Y. Onzuka, M. Itagaki, H. Hirota and Y. Yamamoto, *Organometallics*, 1994, **13**, 2800. W. Satoh, R. Nadano, Y. Yamamoto and K.-y. Akiba, *Chem. Commun.*, 1996, 2451; W. Satoh, R. Nadano, G. Yamamoto, Y. Yamamoto and K.-y. Akiba, *Organometallics*, 1997, **16**, 3664.

6 For similar fluoride transfer: K. M. Kadish, M. Autret, Z. Ou, K.-y. Akiba, S. Masumoto, R. Wada and Y. Yamamoto, *Inorg. Chem.*, 1996, **35**, 5564.

7 Z. Otwinowski, University of Texas, Southwestern Medical Center. The program is available from Mac Science Co.

Communication 8/09601E