# Synthesis and X-Ray Structures of Arsenic(V) Porphyrins with Symmetric Diaxial Ligands of $Me_2$ and $F_2$

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(Received March 11, 1999; CL-990165)

Arsenic porphyrins $[(TPP)As(Me)_2]^+PF_6^-$ (**2-PF$_6$**), $[(TPP)As(F)_2]^+PF_6^-$ (**3-PF$_6$**), and $[(OEP)As(F)_2]^+PF_6^-$ (**4-PF$_6$**) were prepared and the X-ray crystallographic structures revealed that the axial ligand and the porphyrin core affected to control the conformation of the porphyrins.

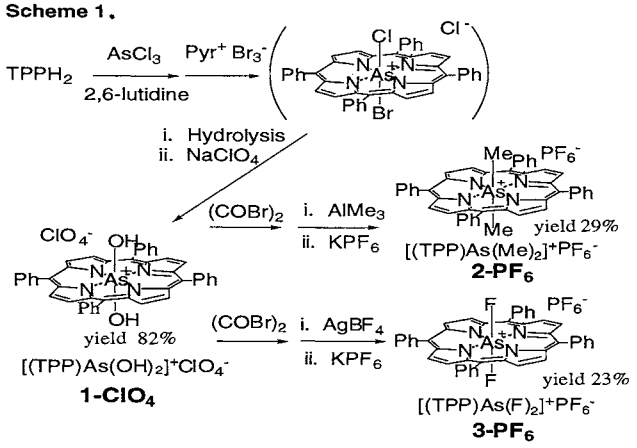
Group 15 element porphyrins have attracted recent interest,[1] but until our recent report on synthesis of arsenic octaethylporphyrins[2] there have been no reliable reports on the synthesis of arsenic porphyrins. The crystal structure of $[(OEP)As(Me)(OH)]^+ClO_4^-$ was the first characterization of arsenic porphyrin by X-ray crystallographic analysis.

Here we report on preparation of arsenic tetraphenylporphyrins and on X-ray crystallographic analysis of $[(TPP)As(Me)_2]^+PF_6^-$ (**2-PF$_6$**), $[(TPP)As(F)_2]^+PF_6^-$ (**3-PF$_6$**), and $[(OEP)As(F)_2]^+PF_6^-$ (**4-PF$_6$**). Interestingly, the porphyrin core of **2-PF$_6$** and **4-PF$_6$** is almost planar in contrast to **3-PF$_6$** which adapts $S_4$ ruffled conformation.

$[(TPP)As(OH)_2]^+ClO_4^-$ (**1-ClO$_4$**)[3] was prepared in 82% yield from $(TPP)H_2$ with excess $AsCl_3$ followed by treatment of pyridinium tribromide and hydrolysis of the resultant $[(TPP)As(Cl)(Br)]^+Br^-$ based on the similar procedures recently reported by us for arsenic octaethylporphyrins.[2] The hydroxy group of **1-Cl** could be converted to the corresponding bromide $[(TPP)As(Br)_2]^+Br^-$ by treatment of **1-Cl** with oxalyl bromide. Trialkylaluminum method, which was developed for introduction of alkyl groups into antimony and phosphorus octaethylporphyrins,[4,5] also worked for the arsenic tetraphenylporphyrin. $[(TPP)As(Me)_2]^+PF_6^-$ (**2-PF$_6$**)[6] was obtained in 29% yield by the reaction of $[(TPP)As(Br)_2]^+Br^-$ with trimethylaluminum followed by counteranion exchange.

$[(TPP)As(F)_2]^+PF_6^-$ (**3-PF$_6$**, 23% yield)[6] and $[(OEP)As(F)_2]^+PF_6^-$ (**4-PF$_6$**, 81% yield)[6] were obtained by the reaction of the corresponding bromides with $AgBF_4$ followed by counteranion exchange (Scheme 1).

**Scheme 1.**




These arsenic porphyrins are stable to atmospheric moisture and chromatographic treatment. The characteristic methyl signal was observed in **2-PF$_6$** at very high field (δ -5.39 (s, 6H)) due to large ring current effect of the porphyrin nucleus.[2,7]

Crystals of **2-PF$_6$** and **3-PF$_6$** were obtained by recrystallization from dichloromethane-di-*n*-butyl ether.[8] X-ray structural analysis of **2-PF$_6$** shows that the As atom is on a crystallographic symmetry center. The ORTEP drawings of **2-PF$_6$** and **3-PF$_6$** are shown in Figures 1 and 2. Selected bond distances around the arsenic atom are listed in note 8. Each of the geometries about the arsenic atom is distorted octahedral. Interestingly, the porphyrin core of **2-PF$_6$** is almost planar in contrast to $S_4$ ruffled conformation of **3-PF$_6$**. The averaged As-N bond distance is much shorter in $[(TPP)As(F)_2]^+PF_6^-$ (**3-PF$_6$**: 1.927(2) Å) than that in $[(TPP)As(Me)_2]^+PF_6^-$ (**2-PF$_6$**: 2.062(2) Å). The degree of ruffling of the core (Δr: Å) in **3-PF$_6$** is calculated by root mean square of the deviation of the 24 atoms[9] to be 0.427 and that of **2-PF$_6$** as 0.035.

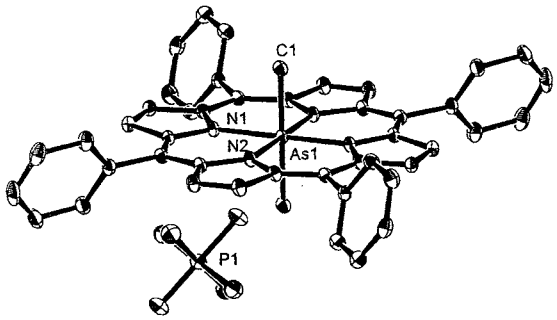



**Figure 1.** ORTEP drawing of **2-PF$_6$** (30% thermal ellipsoid).

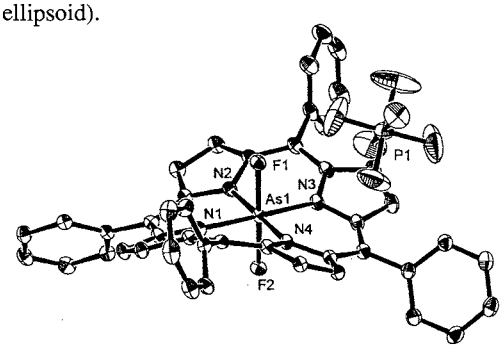



**Figure 2.** ORTEP drawing of **3-PF$_6$** (30% thermal ellipsoid).

Based on the structural analysis of a variety of the phosphorus octaethylporphyrins $[(OEP)P(X)(Y)]^+Z^-$,[5] it could be concluded that as the axial ligands (X and Y) became more electronegative the degree of ruffling became greater and the averaged P-N bond distance became shorter. Therefore, the electronic effect of the axial substituents plays a major role here in

determining the degree of ruffling and the averaged As-N bond distance.

Also, we observed the presence of clear threshhold distance (ca. 1.95 Å) of the phosphorus and the nitrogen bond between the extensively ruffled porphyrin core ($[(OEP)P(Et)(NEt_2)]^+ ClO_4^-$: av. P-N bond, 1.92(1) Å; Δr= 0.381 Å) and the planar one ($[(OEP)P(Me)_2]^+PF_6^-$: av. P-N bond, 1.990(8) Å; Δr= 0.128 Å).[5] This is also the case for arsenic tetraphenylporphyrins, i.e., **3-PF6** is ruffled and **2-PF6** is planar.

It is interesting to mention here that the structure of the corresponding arsenic octaethylporphyrin, $[(OEP)As(F)_2]^+PF_6^-$ (**4-PF6**, Δr= 0.024 Å) was found to be planar and the averaged As-N bond distance (1.966(1) Å) was longer than the threshold value (1.95 Å).

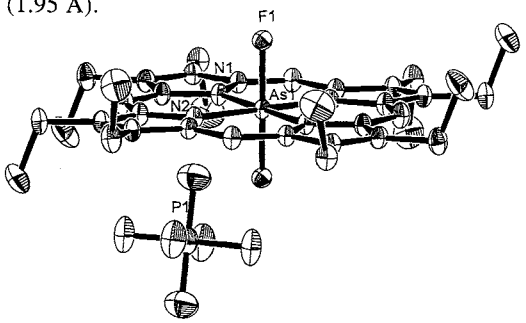



**Figure 3.** ORTEP drawing of **4-PF6** (30% thermal ellipsoid).

Although the slightly shorter M-N bond distances in metallotetraphenylporphyrins than that of the corresponding octaethylporphyrins have been reported for some metalloporphyrins,[10] such large electronic effects of the porphyrin core to change the fundamental conformations have never been observed and we are now very much interested in the electronic effect of porphyrin cores.

## References and Notes


1 for recent examples: a) H. Segawa, K. Kunimoto, K. Susumu, M. Taniguchi, and T. Shimidzu, *J. Am. Chem. Soc.*, **116**, 11193 (1994). b) T. Shiragami, K. Kubomura, D. Ishibashi, and H. Inoue, *J. Am. Chem. Soc.*, **118**, 6311 (1996). c) T. Barbour, W. J. Belcher, P. J. Brothers, C. E. F. Rickard, and D. C. Ware, *Inorg. Chem.*, **31**, 746 (1992). d) P. Sayer, M. Gouterman, and C. R. Connell, *Acc. Chem. Res.*, **15**, 73 (1982).

2 a) W. Satoh, R. Nadano, Y. Yamamoto, and K.-y. Akiba, *Chem. Commun.*, **1996**, 2451. b) W. Satoh, R. Nadano, G. Yamamoto, Y. Yamamoto, and K.-y. Akiba, *Organometallics*, **16**, 3664 (1997).

3 Preparation of **1-ClO4**: To a solution of $(TPP)H_2$ (200 mg, 0.325 mmol) in dry dichloromethane (20 mL) was added 2,6-lutidine (0.4 mL) and arsenic trichloride (0.68 mL, 8.08 mmol) at room temperature under Ar. The mixture was stirred at room temperature for 12 h. Pyridinium tribromide (120 mg, 0.375 mmol) was added and the mixture was stirred at room temperature for 3 days. Compound **1-Cl** (202 mg, yield 82%) was obtained in a pure form after chromatography [neutral $Al_2O_3$, benzene/ethyl acetate/ methanol (15:15:1)]. Counteranion exchange of **1-Cl** with sodium perchlorate gave **1-ClO4** quantitatively. **1-ClO4**: $^1$H NMR ($CDCl_3$): δ 7.74-7.79 (m, 12H), 8.16-8.19 (m, 8H), 9.11 (s, 8H). UV ($CH_2Cl_2$) λ (log ε) 309 (4.38), 422 (5.64), 551 (4.38), 591 (4.05). Elemental analysis of **1 ~ 4** gave correct results.

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6 Data: **2-PF6**; $^1$H NMR ($CDCl_3$): δ -5.39 (s, 6H), 7.87-7.89 (m, 12H), 8.28-8.29 (m, 8H), 9.29 (s, 8H). UV ($CH_2Cl_2$) λ (log ε) 338 (4.48), 437 (5.62), 576 (4.26), 618 (4.44). **3-PF6**: $^1$H NMR ($CDCl_3$): δ 7.86-7.88 (m, 12H), 8.11-8.12 (m, 8H), 9.39 (s, 8H). $^{19}$F NMR ($CDCl_3$): δ -25.47 (s, 2F), -74.39 (d, 6F). UV ($CH_2Cl_2$) λ (log ε) 310 (4.20), 421 (5.59), 549 (4.29), 591 (3.75). **4-PF6**: $^1$H NMR ($CDCl_3$): δ 1.98 (t, 24 H), 4.21 (q, 16 H), 10.30 (s, 4 H). UV ($CH_2Cl_2$) λ (log ε) 366 (4.60), 424 (5.45), 551 (4.23), 585 (3.86).

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8 Crystal data: **2-PF6**; $C_{46}H_{34}N_4PF_6As$, M = 862.7, monoclinic, space group $P2_1/n$, $a$ = 10.7910(4), $b$ = 8.0240(2), $c$ = 21.6390(8) Å, $\beta$ = 94.794(2) deg, $V$ = 1867.10(10) Å$^3$, $Z$ = 4, $Dc$ = 1.53 g cm$^{-3}$, $T$ = 190 K, $R$ = 0.046, $Rw$ = 0.054 for 3562 reflections ($I > 3\sigma(I)$). Selected bond distances (Å): As-N1 2.062(2), As-N2 2.062(2), As-C1 1.953(3). **3-PF6**; $C_{44}H_{28}N_4PF_8As$, M = 870.6, monoclinic, space group $P2_1/n$, $a$ = 17.7710(4), $b$ = 9.7020(2), $c$ = 21.5370(5) Å, $\beta$ = 101.637(1) deg, $V$ = 3637.0(1) Å$^3$, $Z$ = 4, $Dc$ = 1.61 g cm$^{-3}$, $T$ = 180 K, $R$ = 0.052, $Rw$ = 0.058 for 7357 reflections ($I > 3\sigma(I)$). Selected bond distances (Å): As-N1 1.935(2), As-N2 1.925(2), As-N3 1.930(2), As-N4 1.917(2), As-F1 1.745(2), As-F2 1.751(2). **4-PF6**; $C_{35}H_{36}N_4PF_8As$, M = 790.6, triclinic, space group $P\bar{1}$, $a$ = 7.7710(8), $b$ = 8.8060(6), $c$ = 14.173(1) Å, $\alpha$ = 91.132(6) deg, $\beta$ = 97.832(4) deg, $\gamma$= 113.000(5) deg, $V$ = 881.5(1) Å$^3$, $Z$ = 1, $Dc$ = 1.48 g cm$^{-3}$, $T$ = 297 K, $R$ = 0.047, $Rw$ = 0.052 for 3300 reflections ($I > 3\sigma(I)$). Selected bond distances (Å): As-N1 1.961(1), As-N2 1.971(1), As-F1 1.731(1).

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