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Synthesis and characterization of per/polyfluorophenoxy derivatives of octachlorocyclotetraphosphazenes

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Abstract

Octachlorocyclotetraphosphazene was treated with various fluorinated phenols to form partially and completely substituted cyclotetraphosphazenes. The mono-substitution reactions were carried out using a base in benzene while for complete substitution sodium salts of the corresponding phenoxides were used. All compounds were characterized by ^{1}H, ^{19}F, and ^{31}P NMR, IR and mass spectroscopic methods. A crystal structure was obtained for $N_4P_4(OC_6F_5)_8$, and shows that the phosphazene ring is puckered. The angle of the planes N2P2N1P1N4 to N4P4N3P3N2 is 45.5° and the angle of the planes N1P1N4P4N3 to N3P3N2P2N1 is 43.8°. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Phosphazene; Tetramer; Fluoroalkoxide; Single crystal analysis

1. Introduction

Cyclotriphosphazenes (**I**), (Fig. 1) are one of the most well studied inorganic heterocyclic systems known [1]. The linear analogue polyphosphazenes (**II**) are well known for their use as membranes, polymer solid electrolytes, drug carriers, and flame retardants, etc. [2]. Although studies of the cyclic trimer and the linear polyphosphazenes have been well documented, the cyclotetraphosphazene (**III**) systems have not been well studied. Cyclotriphosphazenes containing fluorinated phenoxy groups are useful as lubricants and for surface coatings in magnetic tapes and other end use applications [3,4]. The ultimate focus of our research is the preparation of organic polymers containing cyclotetraphosphazenes as pendant groups [5] and the characterization of these materials as surface coatings. In this study we report the synthesis and characterization of mono-, di-, and octa-substituted fluorophenoxycyclotetraphosphazenes. Some of these compounds have been reported previously but were poorly characterized [6].

2. Experimental

2.1. Materials

Octachlorocyclotetraphosphazene (Otsuka Chemical Co., Ltd., Japan) was sublimed and recrystallized prior to use. Sodium hydride, triethylamine, *p*-fluorophenol, pentafluorophenol, *p*-trifluoromethyl-phenol (Aldrich) were used as received. 4-Hydroxy-4′-vinylbiphenyl was synthesized according to [13].

2.2. Methods

^{1}H and ^{19}F NMR spectra were obtained on a Bruker AC200 or Bruker AC300 instrument in $CDCl_3$ solvent. Chemical shift values were reported relative to TMS and CCl_3F for proton and fluorine, respectively. Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer with KBr disks. Mass spectral data (EI, FAB^+, and accurate mass) were obtained using a Jeol JMS AX505HA mass spectrometer.

2.2.1. X-ray diffraction studies

The X-ray diffraction data for compound **5** was collected on a Siemens SMART diffractometer with a CCD detector at −90 °C. Data collection parameters are listed in Table 1. The frame data were acquired with the SMART [14–17] software using a Siemens three-circle platform using Mo Kα radiation ($\lambda = 0.71073$ Å) from a fine-focus tube. The χ-axis on this platform is fixed at 54.74°, and the diffractometer is equipped with a CCD detector maintained near −54 °C. Cell constants are determined from 60, 10 s, frames. A complete hemisphere of data is scanned on ω (0.3°) with a run time of 10 s per frame at a detector resolution of 512 × 512 pixels. A total of 1271 frames were collected in three sets, and a final set of 50 frames, were also

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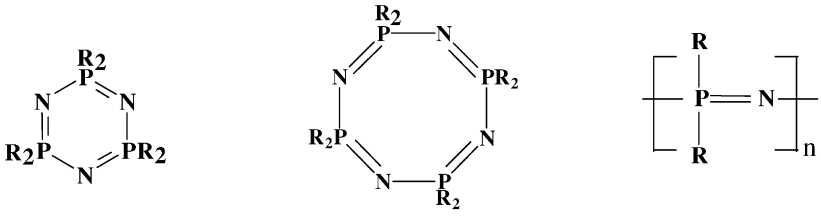


Fig. 1. Phosphazene structures.

collected to determine the crystal decay. The frames were then processed on a SGI-Indy/Indigo 2 workstation using SAINT software, to give the *hkl* file corrected for Lp/decay. The structure was solved by the direct method using the SHELX-90 program and refined by a least squares method on F^2, SHELX-93, incorporated in SHELXTL-PC Version 5.03.

2.2.2. Synthesis of $N_4P_4Cl_7$–OC_6H_4–C_6H_4–$CH{=}CH_2$ (1)

To a stirred solution of dry benzene containing octachlorocyclotetraphosphazene (2.0 g, 4.3 mmol), a solution of 4-hydroxy-4′-vinyl-biphenyl (0.84 g, 4.3 mmol) and triethylamine (0.4g, 4.3 mmol) in dry benzene was added slowly over a period of 30 min at room temperature. The reaction mixture was stirred for an additional 3 h. After removing the triethyl amine hydrochloride formed in the reaction, the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel using hexanes:methylene chloride in a 4:1 ratio to afford the product (**1**) as a white solid (yield, 44%). Melting point (mp) 65 °C. MS (EI+) (species, intensity): 622 (M^+, 100); accurate mass (EI+): 621.7679, 623.7644 (found) and 621.7674, 623.7645 (calculated); ^{31}P NMR (δ, ppm): −4.0 to −5.8 (mult), −10.7 (t, –P(OR)Cl, $J = 34$ Hz); ^{1}H NMR (δ, ppm): 7.7–7.2 (m, biphenyl, 8H); 6.8 (dd, –CH, 1H, $J = 14$ Hz); 5.8 (d, –CH_2, 1H, $J = 9$ Hz); 5.3 (d, –CH_2, 1H, $J = 5$ Hz); IR (KBr, cm^{-1}): 1493(s); 1337 (vs); 1305 (vs); 1224 (s); 1196 (s); 1166 (s); 1019 (m); 970 (vs); 914 (m); 827 (s); 784 (m); 758 (m); 706 (m); 642 (m); 590 (vs); 575 (vs); 508 (vs).

Table 1
X-ray crystal data and intensity collection parameters for compound **5**

Empirical formula	$C_{48}F_{40}N_4O_8P_4$
Color	Colorless
Cryst size (mm)	0.38 × 0.15 × 0.05
Cryst system, space group	Orthorhombic, *Pbca*
Unit cell dimension	
a (Å)	24.0675(4)
b (Å)	17.6226(0)
c (Å)	26.1115(0)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	11074.7(2)
Z	8
ρ_{calc} (Mg m^{-3})	1.972
F(0 0 0)	6400
Absorption coefficient (mm^{-1})	0.406
Temperature (K)	183(2)
θ_{max} (°)	22.50
Number of reflections collected	66517
Final indices (2δ data), $R1$($wR2$)	0.0912(0.1384)
All data, $R1$($wR2$)	0.1487(0.1594)
Goodness-of-fit, $S(F^2)$	1.100
Largest difference peak (electron Å^{-3})	0.278
Largest difference hole (electron Å^{-3})	−0.322

2.2.3. Synthesis of $N_4P_4Cl_7$(OC_6H_4F-p) (2)

To a stirred solution of benzene containing 0.4 ml of triethylamine, 1.0 g of octachlorocyclotetraphosphazene and 0.24 g of *p*-fluorophenol were added slowly under nitrogen. The solution was stirred for 16 h at room temperature under nitrogen. Benzene was removed and the product was purified with a silica gel column using 3:1 hexane/methylene chloride as mobile phase. The product obtained (**2**) was an oil (0.61 g, 53% yield). MS (EI+) (species, intensity): 538 ($M^+ - 1$, 100); 426 (M^+–OC_6H_4F, 29.1); accurate mass (EI+) *m/z* 539.1966 (found), 539.1869 (calculated); ^{31}P NMR (δ, ppm): −12.0 (t, $J = 40$ Hz); −6.2 (mult); −6.3 (mult); ^{1}H NMR (δ, ppm): 7.3–7.0 (mult); ^{19}F NMR (δ, ppm): −116 (t, $J = 7.5$ Hz); IR (KBr, cm^{-1}): 3082 (w); 2213 (w); 2018 (m); 1873 (w); 1641 (w); 1599 (w); 1502 (s); 1309 (vs); 1175 (vs); 1090 (m);1006 (w); 972 (s); 925 (w); 903 (m); 837 (s); 785 (m); 727 (m); 707 (m); 685 (m); 634 (w); 605 (vs); 497 (vs); 456 (m).

2.2.4. Synthesis of $N_4P_4Cl_6$(OC_6H_4F-p)$_2$ (3)

To a stirred solution of dry THF containing 0.07 g of sodium hydride, 0.36 g of *p*-fluorophenol in dry THF was added slowly under nitrogen. The resulting solution was added slowly to 1.0 g of octachlorocyclotetra-phosphazene in dry THF. The reaction mixture was allowed to stir for 16 h at room temperature under nitrogen. THF was removed and the product was purified using a silica gel column with 5:1 hexane/methylene chloride mobile phase. The product (**3**) was obtained as an oil (0.47 g, 35% yield). MS (EI+) (species, intensity): 613 (M^+, 39), 503 (M^+–OC_6H_4F, 100); accurate mass (EI+): 614.8375 (found), 614.8300

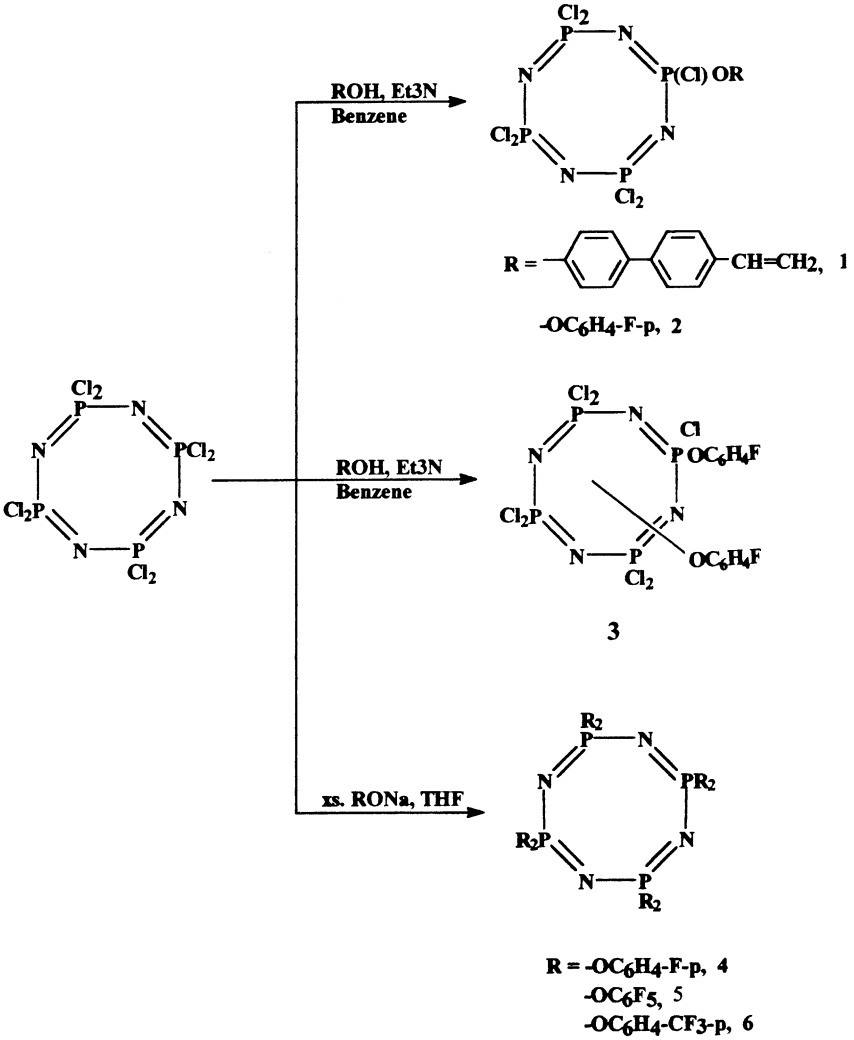
(calculated); ^{1}H NMR (δ, ppm); 7.3–7.0 (mult); ^{19}F NMR (δ, ppm): −116 (s); IR (KBr, cm^{-1}) 3083 (w); 2889 (w); 2360 (w); 2331 (w); 2239 (w); 2023 (w); 1874 (m); 1734 (w); 1642 (w); 1600 (m); 1501 (s); 1318 (vs); 1175 (vs); 1091 (m); 1011 (m); 966 (s); 927 (m); 909 (m); 782 (m); 726 (m); 708 (m); 683 (m); 635 (m); 592 (s); 510 (s).

2.2.5. Synthesis of $N_4P_4(OC_6H_4F\text{-}p)_8$ (**4**)

To a stirred solution of dry THF containing 0.11 g of sodium hydride, 0.48 g of *p*-fluorophenol in dry THF was slowly added under nitrogen. The resulting sodium phenoxide was added slowly to 0.25 g of octachlorocyclotetraphosphazene in dry THF. The reaction mixture was refluxed for 16 h under nitrogen. THF was removed and the product was purified using a silica gel column with a 2:1 hexane:-methylene chloride mobile phase. This gave (**4**) as a white solid (0.31 g, 54%). Accurate mass (EI+): 1068.1213 (found), 1068.1043 (calculated); ^{31}P NMR (δ, ppm) −11.5 (s); ^{1}H NMR (δ): 6.8 (mult), 1.3 (s), 0.9 (mult); ^{19}F NMR (δ, ppm); −118 (mult); IR (KBr, cm^{-1}): 3119 (m); 3083 (m); 2926 (m); 2562 (w); 2418 (w); 2331 (w); 2033 (w); 1948 (w); 1872 (m); 1641 (m); 1602 (m); 1496 (s); 1366 (vs); 1346 (vs); 1229 (vs); 1179 (vs); 1090 (s); 945 (vs); 826 (vs); 791 (s); 744 (m); 718 (s); 671 (m); 633 (m); 554 (s).

2.2.6. Synthesis of N_4P_4 $(OC_6F_5)_8$ (**5**)

To a stirred solution of dry THF containing 0.13 g of sodium hydride, 0.99 g of pentafluorophenol in dry THF was slowly added under nitrogen. The resulting sodium phenoxide was added slowly to 0.25 g of octachlorocyclotetraphosphazene in dry THF. The reaction mixture was refluxed for 16 h under nitrogen. THF was removed and the product was purified on a silica gel column with a 3:1 hexane/methylene chloride mobile phase. The product (**5**) was obtained as a white crystaline solid. (0.54 g, 61% yield). MS (EI+) (species, intensity): 1643 (M^{+} 21) 1460 (M^{+}–OC_6F_5, 100), ^{31}P NMR (δ, ppm) −10.9 (s); ^{19}F NMR (δ, ppm) −155 (d, J = 10 Hz), −159 (t, J = 12 Hz), −163 (mult); IR (KBr, cm^{-1}): 3438 (w); 2676 (w); 2470 (w); 2156 (w); 1752 (w); 1513 (s); 1482 (m); 1356 (s); 1308 (s); 1153 (s); 1025 (vs); 889 (m); 862 (m); 819 (w); 759 (s); 721 (m); 600 (m); 567 (m).



Scheme 1. Synthetic methods of title compounds.

*2.2.7. Synthesis of N_4P_4 ($OC_6H_4CF_3$-p)$_8$ (**6**)*

To a stirred solution of dry THF containing 0.14 g of sodium hydride, 0.88 g of *p*-trifluoromethylphenol in dry THF was slowly added under nitrogen. The resulting sodium phenoxide was added slowly to 0.25 g of octachlorocyclotetraphosphazene in dry THF. The reaction mixture was allowed to stir at room temperature for 16 h under nitrogen. THF was removed and the product was purified using a silica gel column with a 2:1 hexane/methylene chloride mobile phase. The product (**6**) was obtained as a white solid (0.53 g, 67%). MS (EI+) (species, intensity) 1468 ($M^+ - 1$, 25), 1306 (M^+–$OC_6H_4CF_3$, 100); accurate mass (EI+): 1468.7518 (found), 1468.7514 (calculated); ^{31}P NMR (δ, ppm) −13.5 (s); ^{19}F NMR (δ, ppm) −62.6 (s); IR (KBr, cm^{-1}): 3086 (w); 1909 (w); 1781 (w); 1614 (s); 1513 (s); 1315 (vs); 1104 (vs); 1069 (s); 1018 (m); 964 (vs); 845 (s); 798 (m); 772 (m); 729 (m); 655 (s); 638 (m); 589 (m); 543 (m).

3. Results and discussion

Scheme 1 shows the synthetic methods used to prepare the title compounds.

For the mono- and di-substituted products, triethylamine was used as a hydrogen chloride scavenger. Complete substitution of the chlorine present in the tetramer was achieved by using the sodium salt of the corresponding phenoxides. Compounds **1**, **4**–**6** were obtained as colorless solids while **2** and **3** were viscous oils. Yields of **4**–**6**, where excess phenoxide was employed, were all high. The mono- and di- substituted *p*-fluorophenoxy derivatives were obtained in low yields after purification using a silica gel column. The reason for the low yields is related to the reactivity of the P–Cl bonds. After substitution of one of the chlorines, the remaining P–Cl bonds become very reactive giving multiply substituted products. Also, due to its structural flexibility, the eight-membered ring is significantly more reactive than the planar six-membered trimer [6,7]. Several minor multiply substituted products were separated from the main products in each reaction via thin layer chromatography (TLC) using hexanes and methylene chloride in a 5:1 ratio on silica gel columns.

The phosphazene tetramers were characterized by multinuclear NMR, IR, and mass spectral techniques. ^{31}P NMR showed three different phosphorus atoms in a AB2X complex spectrum for **1**. An up-field chemical shift centered at −10.7 ppm from the starting material (−6.9 ppm) was assigned to the biphenylyloxy substituted phosphorous atom. The two phosphorous atoms adjacent to the substituted phosphorous and the fourth phosphorus atom showed complex multiplets centered at approximately −4.8 ppm (Fig. 2). The same spectral pattern was obtained for compound **2**, the singly substituted *p*-fluorophenoxy derivative.

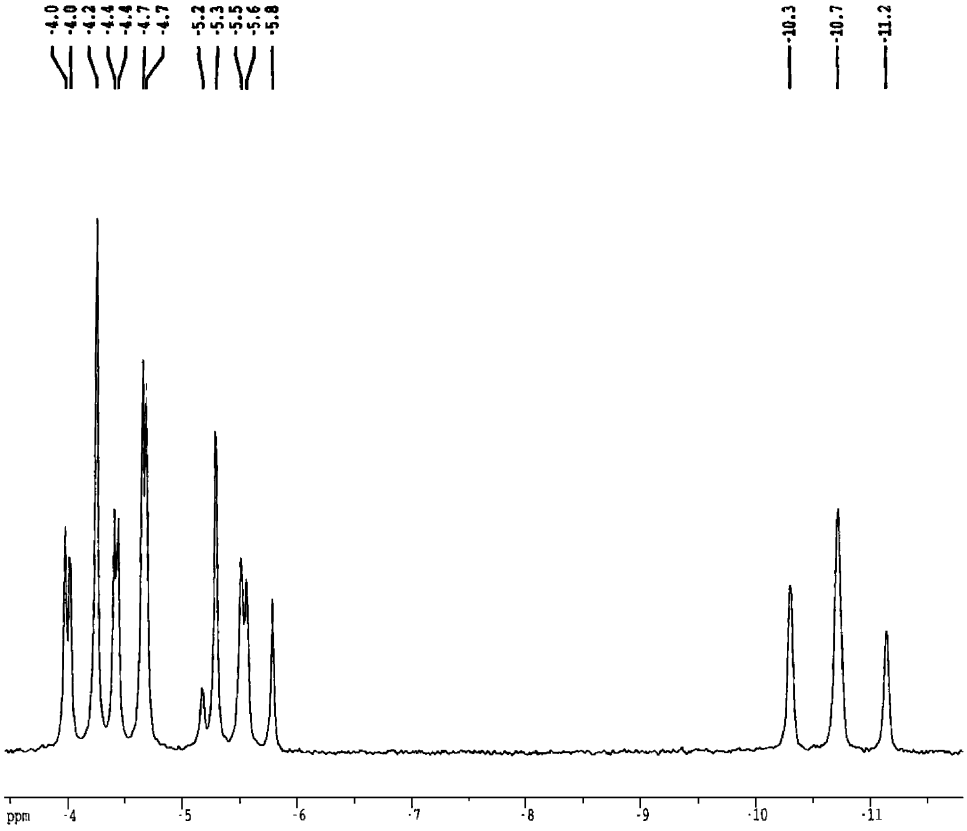


Fig. 2. ^{31}P NMR spectra for $N_4P_4Cl_7$–OC_6H_4–C_6H_4–CH=CH_2 (**1**).

Previous studies reported in the literature have also explored the chemistry of the complete replacement of chlorine by fluoroalkoxy groups on cyclophosphazenes [8–10]. Several studies on these reactions using various equivalents of the substituting group showed such replacements occur at non-geminal chlorine atoms [8,11]. Our experience in this study is consistent with these earlier reports. For example, mass spectral data obtained for product **3** indicates non-geminal substitution. While it is expected that the electron-accepting character of fluoroalkoxy groups would favor geminal nucleophilic substitution, the substitution pattern seen is likely due to strengthening of the P–Cl bonds as a result of the electron pairs on oxygen [8].The single crystal X-ray experimental parameters for compound **5** are given in Table 1. Table 2 shows selected bond angles and bond distances. The P–N–P bond angles were 133.2(4), 133.1(4), 133.8(4), and 136.4(4)°. Bond angles found for the N–P–N bonds are 123.8(3), 122.5(3), 123.3(3), and 120.7(3)°. These values are greater than those found for the trimeric system $N_3P_3(OC_6H_4F\text{-}p)_6$ [12]. The average P–O bond distance of 1.589 Å was similar to what was found in the case of $N_3P_3(OC_6H_4F\text{-}p)_6$ [12]. The O–P–O bond angles [105.2(3), 101.7(3), 104.0(3), and 100.0(3)°] were significantly larger than those found in the *p*-fluorphenoxy trimer, i.e. 98.9(1), 94.7(2) and 99.2(1)°. The angle of the planes N2P2N1P1N4 to N4P4N3P3N2 is 45.5°. and the angle of the planes N1P1N4P4N3 to N3P3N2P2N1 is 43.8° (Fig. 3).

Table 2
Selected bond lengths (Å) and bond angles (°) for $N_4P_4(OC_6F_5)_8$ (**5**)

N1–P2	1.557(6)
N1–P1	1.562(6)
N2–P3	1.554(6)
N2–P2	1.560(6)
N3–P3	1.542(6)
N3–P4	1.572(6)
N4–P4	1.557(6)
N4–P1	1.559(6)
O1–P1	1.589(5)
O2–P1	1.582(5)
O1–P2	1.593(5)
O2–P2	1.584(5)
O1–P3	1.595(5)
O2–P3	1.587(5)
O1–P4	1.600(6)
O2–P4	1.583(5)
P2–N1–P1	133.2(4)
P3–N2–P2	133.1(4)
P3–N3–P4	133.8(4)
P4–N4–P1	136.4(4)
O2–P1–O1	105.2(3)
O4–P2–O3	101.7(3)
O6–P3–O5	104.0(3)
O8–P4–O7	100.0(3)
N1–P1–N4	123.8(3)
N1–P2–N2	122.5(3)
N3–P3–N2	123.3(3)
N4–P4–N3	120.7(3)

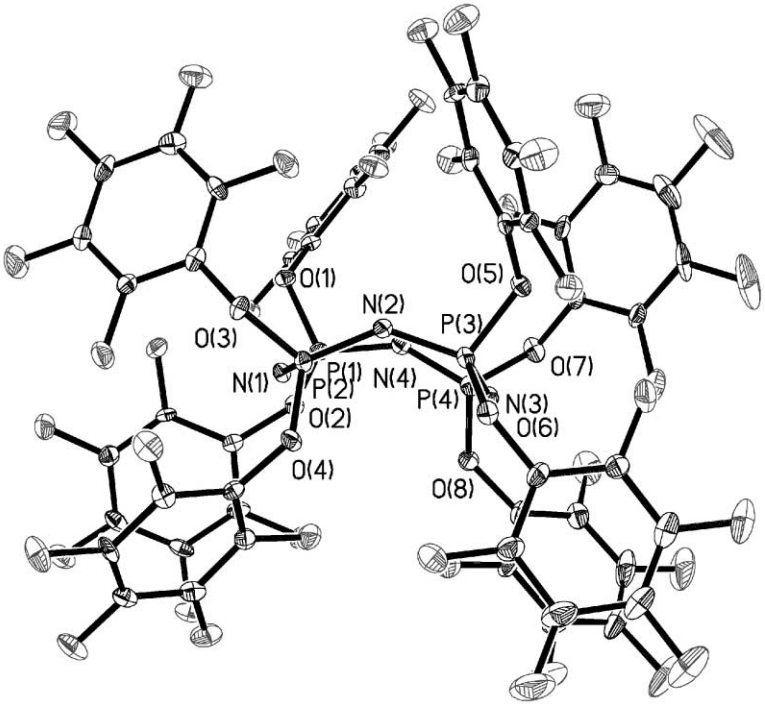


Fig. 3. Crystal structure of $N_4P_4(OC_6F_5)_8$ (**5**)

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