REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE Feb. 19, 1996

3. REPORT TYPE AND DATES COVERED Technical

4. TITLE AND SUBTITLE

Small-Molecule Phosphazene-Substituted Phenoxy Side Groups Synthesis, X-ray Structures, and Comparisons with the Corresponding High Polymers

5. FUNDING NUMBERS

N00014-91-J-1194
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R&T Code: 3132007

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Prepared for publication in Journal of the Chemical Society (Dalton)

12a. DISTRIBUTION/AVAILABILITY STATEMENT

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12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

A series of new cyclic phosphazenes and a linear short chain phosphazene have been synthesized as models for the preparation of the corresponding high polymers. Several of the high polymers were also prepared. The small-molecule compounds were characterized by a combination of ^{31}P NMR, mass spectrometry, and elemental analysis. The crystal and molecular structures of hexakis(4-methylphenoxy)cyclotriphosphazene, hexakis(4-hydroxyphenoxy)cyclotriphosphazene, hexakis(4-benzyloxyphenoxy)cyclotriphosphazene, octakis(4-phenoxyphenoxy)cyclotetraphosphazene, and (t-butylphenoxy)diphosphorus were investigated by single crystal X-ray diffraction techniques.

19960301 064

14. SUBJECT TERMS

Polymers, small-molecule models, phosphazenes, high refractive index.

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified

20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std Z39-18
298-102

OFFICE OF NAVAL RESEARCH

Grant No. N00014-91-J-1194

R&T Project 3132007

Dr. Kenneth J. Wynne, Program Manager

Technical Report No. 30

SMALL-MOLECULE PHOSPHAZENE-SUBSTITUTED PHENOXY SIDE GROUPS: SYNTHESIS, X-RAY STRUCTURES, AND COMPARISONS WITH THE CORRESPONDING HIGH POLYMERS

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Prepared for Publication in *the Journal of the Chemical Society (Dalton)*

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February 19, 1996

Small-Molecule Model Phosphazenes with Para Substituted Phenoxy Side Groups: Synthesis, X-Ray Structures and Comparisons with the Corresponding High Polymers

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A series of new cyclic phosphazenes and a linear short-chain phosphazene have been synthesized as models for the preparation of the corresponding phosphazene high polymers. Several of the high polymers were also prepared. The small molecule compounds were characterized by a combination of ^{31}P NMR, mass spectrometry and elemental analysis. The crystal and molecular structures of hexakis(4-methylphenoxy)cyclotriphosphazene (**2a**), hexakis(4-hydroxyphenoxy)cyclotriphosphazene (**2b**), hexakis(4-phenoxyphenoxy)cyclotriphosphazene (**2e**), hexakis(4-benzyloxyphenoxy) cyclotriphosphazene (**2f**), octakis(4-phenoxyphenoxy)cyclotetraphosphazene (**4a**) and (t-butylphenoxy)diphosphorus short chain (**6a**) were investigated by single crystal x-ray diffraction techniques. Crystals of **2a** are triclinic of space group $P\bar{1}$, with a = 9.790(1) Å, b = 11.399(4) Å, c = 18.495(2) Å, α = 97.86(2)°, β = 95.33(1)°, γ = 102.85(1)° and Z = 2. Crystals of **2b** are triclinic of space group $P\bar{1}$ with a = 9.577(5) Å, b = 10.148(2) Å, c = 20.395(6) Å, α = 77.66(2)°, β = 85.45(3)°, γ = 84.03(2)°, and Z = 2.Crystals of **2e** are triclinic of space group $P\bar{1}$, with a = 15.348(2) Å, b = 15.567(3) Å, c = 16.035(2) Å, α = 72.02(1)°, β = 66.55(1)°, γ = 59.87(1)° and Z = 2. Crystals of **2f** are triclinic of space group $P\bar{1}$ with a = 9.297(5) Å, b = 15.551(4) Å, c = 23.342(4) Å, α = 84.12(2)°, β = 89.44(3)°, γ = 80.55(2)°, and Z = 2. Crystals of **4a** are triclinic of space group $P\bar{1}$ with a = 16.727(1) Å, b = 20.516(9) Å, c = 25.760(2) Å, α = 106.04(2)°, β = 93.55(6)°, γ = 101.33(7)°. Due to two different crystal conformations in the **4a** unit cell, Z = 4. Crystals of **6a** are triclinic of space group $P\bar{1}$ with a = 13.058(5) Å, b = 14.464(2) Å, c = 14.840(11) Å, α = 70.07(3)°, β = 84.38(4)°, γ = 74.55(3)°, and Z = 2. High polymers, $[NP(OC_6H_4OC_6H_5)_2]_n$, $[NP(OC_6H_4OCH_2C_6H_5)_2]_n$, $[NP(OC_6H_4C(C_6H_5)_3)_2]_n$, $[NP(OCH_2C_6H_4OCH_2C_6H_5)_2]_n$ and $[NP(OC_6H_4C(CH_3)_3)_2]_n$ were also prepared and their structures confirmed by a variety of techniques including ^1H and ^{31}P NMR, elemental analysis and differential scanning calorimetry (DSC).

Introduction.

Aryloxy-substituted phosphazene high polymers are of interest as high-refractive glasses[1,2], liquid crystalline[3-7], non-linear optical[8], and ferroelectric species[9] and, in some cases, as photoreactive polymeric materials.[10-17] The optical properties, in particular, are affected by the groups linked to the phenoxy side groups. For example, phenylphenoxy side groups generate high refractive index materials; and a polymer with 4-iodo-4-phenylphenoxy side units has a refractive index as high as 1.664.[2] The mechanical properties of the polymers also depend on the nature of the units linked to phenoxy side groups and on the presence of one-, two-, or more different co-substituent groups attached to the phosphazene backbone.

Polymers of this type are prepared by replacement of the halogen atoms in poly(dichlorophosphazene), $[NPCl_2]_n$, by reactions with aryloxides[18-21], with the ease of substitution being dependent on both the steric and electronic characteristics of the aryloxy units. Thus, bulky or electronically deactivated nucleophiles under mild reaction conditions, may replace only a fraction of the available chlorine atoms, and require a subsequent treatment with a second, more reactive, nucleophile in order to ensure the absence of hydrolytically sensitive P-Cl units in the final polymer.

Macromolecular substitution reactions are more complicated than the corresponding reactions at the small molecule level. In a typical macromolecular reaction, the replacement of 30,000 chlorine atoms per polymer molecule must be induced. Hence, a prudent protocol in this type of research is to examine prospective polymer reactions first at the small-molecule model compound level. The small molecule systems allow characterization by NMR spectroscopy, mass spectrometry and x-ray techniques that are difficult or impossible for high polymers.

In this paper, we discuss the reactions of the model cyclic trimer **1** with a variety of para-substituted aryloxides. The products are listed in Scheme 1 as species **2a-g**. In addition, a cyclic tetrameric model, **4a**, was prepared by the route shown in Scheme 2. In one case, **6a**, a linear short chain phosphazene compound was also prepared and studied as a model for the corresponding high polymer. Several of the same substitution reactions were also investigated at the high polymer level.

All the organic substituted products were examined by microanalysis, NMR, and mass spectrometric techniques. Six of these compounds were also studied by single crystal x-ray crystallography. The other three could not be examined by x-ray methods because they did not yield crystals of suitable quality.

Results and Discussion

Synthesis of the Small Molecule Model Compounds. Replacement of all the chlorine atoms in **1** and **3** by all the nucleophiles occurred relatively easily if a high boiling etheric solvent such as dioxane was employed. This suggests that, provided the terminal unit occupies the 4-position of the aryloxy group, the steric hindrance effects are comparable to that of an unsubstituted phenoxy unit. Hence, the transposition of these reactions to the high polymer level should be relatively straightforward, and this was found to be the case (see later).

The reaction sequence used for the synthesis of the cyclotriphosphazenes is outlined in Scheme 1. The cyclic model compounds were prepared by the treatment of hexachlorocyclotriphosphazene (1) with the sodium aryloxides to yield cyclic phosphazenes with 4-methylphenoxy, 4-t-butylphenoxy, 4-triphenoxymethylphenoxy, phenoxyphenoxy, benzyloxyphenoxy, and 4-benzyloxybenzyloxy side units. The cyclic trimer with 4-hydroxyphenoxy side units was prepared by a two step process, with the second step involving the oxidation of methoxy units of [hexakis(4-methoxyphenoxy) cyclotriphosphazene] using BCl_3. In all these and the following reactions, complete replacement of the chlorine atoms by the aryloxy groups occurred and reaction yields ranged from 70 to 85%.

Scheme 1 near here.

The reaction sequence used for the synthesis of a cyclotetraphosphazene is outlined in Scheme 2. The cyclic model compound was prepared by the treatment of octachlorocyclotetraphosphazene (3) with the sodium aryloxide to yield a cyclic phosphazene tetramer with 4-phenoxyphenoxy side units. Complete replacement of chlorine atoms was achieved in this reaction.

Scheme 2 near here.

The reaction sequence for the synthesis of the linear, short chain phosphazene is illustrated in Scheme 3. The preparation of $OPCl_2NPCl_3$ (5) has been described elsewhere.[22-24] The reaction of 5 with sodium 4-t-butylphenoxide yielded product **6a**. Complete replacement of the chlorine atoms was achieved in this reaction

Scheme 3 near here

Structural Characterization of the Small Molecule Cyclic and Linear Phosphazenes. Species **2(a-g)**, **4(a)** and **6(a)** were characterized by a combination of ^{31}P NMR spectroscopy, mass spectrometry, and elemental analysis (Table 1). The ^{31}P NMR spectra of compounds **2(a-g)** and **4(a)** were singlets with the chemical shift position varying with the nature of the substituent group. The presence of a singlet in the ^{31}P NMR is consistent either with full substitution, or with the presence of only one environment for the phosphorus atoms as would be generated by non-geminal partial substitution. Compound **6a** gave an AB spin pattern due to the two different phosphorus environments within the molecule. Infrared spectra contained the absorbances expected for cyclophosphazenes, with maxima in the 1100-1200 cm^{-1} range characteristic of the (P=N) bond. All the compounds, except for **2d,** yielded mass spectra that contained a parent ion consistent with the expected molecular weights. More extensive characterization of compounds **2a, b, e, f, 4a,** and **6a** was obtained from single crystal x-ray diffraction studies. Compounds **2c, d** and **g** were not studied by x-ray diffraction due to the difficulty of obtaining single crystals of sufficiently high quality. A summary of crystal data and intensity collection parameters are listed in Table 2. Individual positional parameters, bond distances and bond angles, and general temperature factors are depicted in Tables 3-20.

Table 1 near here.

Table 2 near here.

Molecular Structure of 2a This structure was solved to an R factor of 8.5%. As shown in Figure 1, the cyclotriphosphazene ring was slightly puckered, with an average P-N bond length of 1.574(4) Å. The average N-P-N ring angle was 117.2(2)°

and the average P-N-P ring angle was 122.5(2)°. The phenoxy rings were normal in all respects with an average P-O-C angle of 124.6(3)°. The p-methyl groups on the phenoxy rings had an average C-C bond distance of 1.510(7) Å. Individual bond distances and angles are shown in Table 3, and the atomic coordinates of **2a** are shown in Table 4.

Figure 1 near here

Tables 3 and 4 near here

Molecular Structure of 2b The structure of the hexakis(p-hydroxyphenoxy) cyclic trimer, **2b**, was solved to an R factor of 5.0%. This system contained 3 molecules of water per unit cell. The six-membered phosphazene ring showed a slight boat distortion from planarity. Six p-hydroxyphenoxy side groups were linked to the phosphorus atoms of the ring (Figure 2) which had an average P-N bond length of 1.579(3) Å. The average N-P-N ring angle was 117.1(2)° with individual angles of 116.2(1)°, 118.1(1)° and 117.1(1)°. The average P-N-P ring angle was 122.5(2)°. The average O-P-O angle was 100.9(1)°. The phenoxy rings were normal in all respects with an average P-O-C angle of 123.2(3)°. The p-hydroxy groups on the phenoxy rings had an average C-O···(H) bond distance of 1.377(4) Å, which is typical for phenolic groups. No evidence was found that the crystal structure was stabilized by hydrogen bonding. Individual bond distances and angles are shown in Table 5, and the atomic coordinates of **2b** are shown in Table 6.

Figure 2 near here

Tables 5 and 6 near here

Molecular Structure of 2e This structure was solved to an R factor of 3.5%. The cyclic trimeric phosphazene ring was slightly puckered in a chair conformation. The average P-N bond length was 1.582(2) Å. The average N-P-N ring angle was 116.7(2)° and the average P-N-P ring angle was 122.3(1)°. The average O-P-O angle was 96.80(8)° with individual angles of 98.39(9)°, 93.16(7)° and 98.86(7)°. The narrowest of these angles was probably due to crystal packing forces. The P-O-C angles ranged from 122.6(2)° to 131.2(1)°, with an average angle of 125.3(2)° and are considered to be normal, as indeed are the C-O-C angles which range from 117.1(2)° to 120.1(2)° with an average value of 118.8(2)°. The aryl rings are planar with normal dimensions. The orientation of the side groups is interesting, with five of the units oriented roughly normal to the phosphazene ring plane (Figure 3) and two disposed approximately parallel to and away from the inorganic ring. The stereo view of the packing diagram (Figure 4) illustrates the way in which the side group torsional flexibility around the P-O-C and C-O-C units allows an efficient use by the side groups of the available unit cell volume. By contrast, earlier structure solutions of $[NP(OC_6H_4C_6H_5)_2]_3$, and analogous short chain species showed that the side group conformation in those species was significantly constrained by the rigidity of the structure.[25] Individual bond distances and bond angles are shown in Table 7, and the atomic coordinates of **2e** are shown in Table 8.

Figures 3 and 4 near here

Tables 7 and 8 near here.

Crystal and Molecular Structure of 2f The structure of **2f** was solved to an R factor of 11.8%. The high R value may be a consequence of the size of each molecule (96 non-hydrogen atoms). The phosphazene ring is almost planar but with a slight chair distortion. The P-N bond distances ranged from 1.54(1) Å to 1.59(1) Å with an average P-N bond distance of 1.575(9) Å. The average N-P-N ring angle was 118.5(6)° and the average P-N-P bond angle was 120.4(7)°. The average O-P-O angle was 95.8(5)°. All the benzenoid rings appear to be normal. The P-O-C angles were within expected limits (average P-O-C angle of 124.2(7)°). So too were the C-O-C angles (in the range of 112.6(6)° to 122.8(8)°) with the exception of one wider angle of 130.6(14)°. Again, crystal packing forces may explain this anomaly. The orientation of side groups (Figure 5) is interesting, with maximum extension of each unit being favored, and with four of the groups oriented almost normal to the phosphazene ring and the remaining two disposed away from the ring at roughly 45°. The packing diagram (Figure 6) further illustrates this structure. Individual bond distances and bond angles are listed in Table 9, and the atomic coordinates of **2f** are shown in Table 10.

Figures 5 and 6 near here

Tables 9 and 10 near here.

Crystal and Molecular Structure of 4a Compound **4a** contains eight phenoxyphenoxy side groups attached to a cyclic, tetrameric phosphazene ring. The x-ray crystal structure of this compound contained two different molecular conformations of **4a**, and the structure was solved to an R factor of 9.9% (This high value could be due to the complexity and size of the molecule as well as the difference in molecular conformation). (Figure 7) In both conformations, the phosphazene ring was puckered into a boat shaped conformation and had an overall average P-N bond length of 1.560(9) Å. Individual P-N bond lengths were 1.56(1) Å, 1.560(9) Å, 1.55(1) Å, 1.531(9) Å, 1.57(1) Å, 1.584(9) Å, 1.55(1) Å, 1.56(1) Å, 1.55(1) Å, 1.560(9) Å , 1.54(1) Å, 1.54(1) Å, 1.587(9) Å, 1.55(1) Å, 1.56(1) Å and 1.56(1) Å. The average N-P-N ring angle was 120.6(6)° with individual values of 120.0(6)°, 120.9(6)°, 120.8(6)°, 120.1(6)°, 120.3(6)°, 121.2(6)°, 121.1(6)° and

120.4(6)°. The average P-N-P ring angle was 135.2(7)° with individual ring angles of 135.4(7)°, 136.2(7)°, 135.9(7)°, 135.2(8)°, 136.4(6)°, 132.8(7)°, 135.4(7)° and 134.4(8)°. The average O-P-O angle was 99.4(5) with individual angles of 99.6(5)°, 98.4(5)°, 98.6(5)°, 100.7(5)°, 99.6(5)°, 99.7(5)°, 98.6(5)° and 100.7(5)°. The phenoxy rings were normal in all respects with an average P-O-C angle of 123.7(7)° and individual values of 124.2(7)°, 124.3(6)°, 123.9(9)°, 124.5(7)°, 123.9(7)°, 123.3(6)°, 126.5(8)°, 121.5(6)°, 122.9(7)°, 124.2(1)°, 123(1)°, 120.9(6)°, 123.8(9)°, 124.2(5)°, 121(1)°, 126.4(9)°. The phenoxyphenol side groups had an average internal C-O-C angle of 118.2(9)° with individual angles of 119(1)°, 119(1)°, 117(1)°, 118.4(9)°, 118(1)°, 120(1)°, 117(1)°, 117(1)°, 117(1)°, 118(1)°, 117.8(9)°, 118(1)°, 118.3(9)°, 119(1)°, 116.3(5)° and 118.3(6)°. As shown in Figure 7, the differences in the conformations arise from twisting within the side groups. In general, the side units extend in a perpendicular manner from the tetramer ring. There appears to be some intramolecular side group stacking or organization within the molecule. Due to the complex nature of the packing diagram (Figure 8), it is difficult to discern stacking between molecules. Individual bond distances and angles are shown in Table 11, and the atomic coordinates of both conformations of **4a** are listed in Table 12.

Figures 7 and 8 near here

Tables 11 and 12 near here

Crystal and Molecular Structure of 6a Compound **6a** is a short-chain linear phosphazene that contains two phosphorus atoms linked to a central nitrogen atom (Figure 9). P(2) was bonded to two 4-t-butylphenoxy groups and an oxygen atom. P(1) was bonded to three 4-t-butylphenoxy groups. The structure was solved to an R factor of 9.1%. The P-N bond distances were not identical. P(1)-N = 1.495 Å and P(2)-N = 1.578 Å. Although different, these are shorter than the single bond value, and this suggests some form of electron delocalization along the P-N skeleton. P(2)-O(6) had a bond length of 1.449 Å, which is shorter than the average P-O bond distances of 1.56 Å. This suggested that P(2)-O(6) has some double bond character. The P-N-P angle assumed a value of 157°, which was wide compared to other short-chain species.[22-24] It is assumed that this reflects the effect of the bulky tert-butyl moiety. The orientation of the side units is probably dictated by the need for each side group to maintain a maximum distance from each other. This effect should also be expected at the high polymeric level. The phenoxy rings appeared normal in all respects and no side group stacking could be detected. Individual bond distances and angles are listed in Table 13, and the atomic coordinates of **6a** are shown in Table 14.

Figure 9 near here

Tables 13 and 14 near here

Synthesis and Characterization of the High Polymers.

Poly(organophosphazenes) containing para substituted phenoxy nucleophiles corresponding to those in compounds **2c**, **d**, **e**, **f** and **g** were also prepared. These high polymers were synthesized under high temperature (150 °C), high pressure conditions, using dioxane as a solvent, in order to favor complete replacement of all the chlorine atoms. These forcing reaction conditions guaranteed a high degree of chlorine replacement, but small amounts of chlorine were still detected in a few cases (0.5% for side group **c**, and 1.2% for **d**). The polymers were characterized by NMR spectroscopy (^1H and ^{31}P), differential scanning calorimetry (DSC) and elemental analysis. Molecular weights were estimated by gel permeation chromatography (GPC) and fell within the range of 1×10^6 to 5×10^6. Glass transition temperatures, determined by DSC, were in the range of 15°C to 50 °C, and ^{31}P NMR shifts for the para substituted phenoxy derivatives were in the range of -15 ppm to -25 ppm .

Conclusions

Phenoxy-substituted phosphazene cyclic trimers and tetramers were some of the earliest organophosphazenes to be synthesized and characterized[26], and a phenoxy-substituted phosphazene high polymer was one of the first stable phosphazenes to be reported.[18-21] Since that time, high polymers with various alkyl and aryl substituent groups linked to the phenoxy side units have played a major role in the industrial development of polyphosphazene elastomers and in the exploration of phosphazenes as structural, fibrous, and optical materials. Yet many of these macromolecular developments have occurred in the absence of fundamental data about the influence of the terminal groups linked to aryloxy units on reaction pathways and molecular conformations.

In this paper, we have shown that, provided the terminal unit is at the para-position of the aryloxide nucleophile, few steric hindrance constraints exist that would limit the number of accessible reactions at the small-molecule level. The preliminary results described here and in recent other papers[1,2] suggest that this situation persists at the level of macromolecular substitution also.

It could be argued that molecular structural information obtained for small-molecule cyclic trimers and tetramers is only of peripheral value for understanding the forces that control conformation and chain packing at the high polymer level. Nevertheless, data from small molecule rings provide virtually the only structural information accessible at this time that can be used to analyze the behavior of high polymers. The use of phosphazene short chains such as **6a** offers information that may be more relevant to linear high polymers, but even here the structural features are probably dominated by the end groups in ways that are not pertinent to molecules that may contain 15,000 or more repeating units for every two end units. The answer clearly lies in the study of longer linear oligomeric phosphazenes, as we have attempted to do in earlier publications[22-24], but these species provide a special challenge with respect to synthesis and crystallization for x-ray studies. Perhaps the most important structural conclusions to be derived from this present paper are related to the orientation of the various aryloxy side groups and their intramolecular interactions. These interactions and the cone-angle volumes swept out by the side units appear to dominate the small-molecule structures, and will presumably exert an even more profound influence on the conformations and packing of the highly flexible long chains found in the macromolecules.

Experimental Section

Analytical Techniques. ^{31}P NMR (^{1}H decoupled) spectra were obtained with the use of a JEOL FX-90Q NMR spectrometer operated at 36.2 MHz. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 at 0 ppm with positive shift values downfield from the reference. Glass transition temperatures (Tg) were recorded with the use of a Perkin Elmer DSC-7 unit equipped with a PE 7500 computer. The samples (10-30 mg) were analyzed in crimped aluminum pans: a heating rate of 40°C/min and a helium flow of 10 ml/min were used. The instrument was calibrated with a cyclohexane standard, with thermal transitions at -87.06 and 6.54°C. Infrared spectra were recorded with the use of a Perkin Elmer Model 283B grating spectrometer, and ion impact mass spectra were obtained with the use of an AEC/MS 902 mass spectrometer. Molecular weight data were obtained with the use of a Hewlett Packard 1090 liquid chromatograph equipped with a HP 1037A refractive index detector with the use of a polystyrene standard. X-ray crystallographic data were collected with the use of an Enraf-Nonius CADIV diffractometer controlled either by a PDP 11/44 computer or by the CAD4PC program installed on a Gateway 2000 386 mb computer. The structures were solved by SDP[27] installed on the PDP 11/44 and also using a SHELX-Multan[28] program installed on the Pennsylvania State University IBM-VMS computer. ORTEP diagrams were generated using Chem3D molecular modeling system software. Elemental analysis were obtained by Galbraith Laboratories, Knoxville, Tennessee.

Materials. Hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene were provided by Ethyl Corporation and was purified by recrystallization from hexane and sublimation at 50 °C (0.05 mmHg). All solvents were dried either over sodium benzophenone ketyl or calcium hydride and were distilled in an atmosphere of dry nitrogen before use. 4-Benzyloxyphenol, 4-benzyloxybenzyl alcohol, p-cresol and 4-methoxy phenol were all obtained from Aldrich, and were purified by sublimation. Boron trichloride was obtained from Aldrich and was used as received. Sodium and sodium hydride (Aldrich) were used as received. All reactions were carried out in an atmosphere of dry nitrogen.

Synthesis of $[NP(OC_6H_4CH_3)_2]_3$ (2a)[29]. $(NPCl_2)_3$ (2.03×10^{-2} mol) in dioxane (150 ml) was added slowly to a stirred solution of sodium p-cresol (2.3×10^{-1} mol) in dioxane (400 ml). The mixture was heated at reflux for 48 h after which time the reaction mixture was cooled and filtered through silica gel. The filtrate was concentrated, dissolved in toluene, and extracted with 1M NaOH (3x) and distilled deionized water (2x). After extraction, the filtrate was concentrated and the remaining residue was recrystallized from hexanes. The product was purified by column chromatography using a dichloromethane eluent.

Synthesis of $[NP(OC_6H_4OH)_2]_3$ (2b)[30]. *(a) Synthesis of $[NP(OC_6H_4OCH_3)_2]_3$:* $(NPCl_2)_3$ (3.4×10^{-2} mol) was dissolved in dioxane (150 ml). To this solution was added a solution of sodium 4-methoxyphenoxide (0.564 mol) in dioxane (600 ml). The mixture was refluxed for 24 h, and was then cooled to room temperature, filtered through silica gel, and concentrated. The oily residue was dissolved in diethyl ether and was extracted with 1M NaOH (3x) and distilled deionized water (3x). The resulting product was recrystallized twice from methanol. *(b) Synthesis of $[NP(OC_6H_4OH)_2]_3$:* $[NP(OC_6H_4OCH_3)_2]_3$ (5.79×10^{-3} mol) was dissolved in 20 ml dry methylene chloride. A boron trichloride solution (150 ml of 1M BCl_3 in CH_2Cl_2) was added by syringe to the trimer solution and the mixture was stirred at room temperature for 48 h. The reaction becomes a dark amber in color. The reaction mixture was then quenched by the addition of methanol and then sodium bicarbonate. The mixture was then gravity filtered and then passed through silica gel and concentrated. The final product was purified by column chromatography using a 1:1 THF/dichloromethane mixture as the eluent.

Synthesis of $[NP(O\text{-}C_6H_4\text{-}{}^tBu)_2]_3$ (2c). $(NPCl_2)_3$ (2.87×10^{-2} mol) in THF (150 ml) was allowed to react with a solution of sodium 4-t-butylphenoxide (3.44×10^{-1} mol), and was boiled at reflux for 12 h. After filtration and reduction of the solvent volume, the crude product was chromatographed through a silica gel column. A dichloromethane/hexane mixture was used as eluent. The product was recrystallized from a dichloromethane/hexane solution.

Synthesis of $[NP(OC_{25}H_{19})_2]_3$ (2d). A solution of $(NPCl_2)_3$ (2.87×10^{-2} mol) in dioxane (75 ml) was added dropwise to a solution of sodium tritylphenoxide (2.3×10^{-2} mol) at 80 °C. The reaction mixture was boiled at reflux for 7 h. The solvent was then removed under reduced pressure and the residual product was extracted with dichloromethane. The product was recrystallized from a dichloromethane/hexane solution.

Synthesis of $[NP(OC_6H_4OC_6H_5)_2]_3$ (2e). A solution of $(NPCl_{23}$ (2.87×10^{-2} mol) in dioxane (20 ml) was added dropwise to a stirred solution of sodium 4-phenoxyphenoxide (2.15×10^{-2} mol) at room temperature. The mixture was refluxed for 20h, and then it was then cooled to room temperature. Filtration and removal of the solvent left an oily product. Purification of the compound was achieved by gradient elution through a silica gel chromatography column with dichloromethane as solvent. The product was recrystallized from toluene and hexane.

Synthesis of $[NP(OC_6H_4OCH_2C_6H_5)_2]_3$ (2f). A solution of $(NPCl_2)_3$ (4.31×10^{-3} mol) in dioxane (25 ml) was added dropwise to a stirred solution of sodium 4-benzyloxy phenoxide (3.6×10^{-2} mol) in dioxane (150 ml). The mixture was boiled at reflux for 17 h, and then it was then cooled to room temperature. Filtration and removal of the solvent left a solid product. Purification of this compound was achieved by gradient elution through a silica gel column with a THF/hexane mixture. The product was recrystallized from a dichloromethane/hexane mixture.

Synthesis of $[NP(OCH_2C_6H_4OCH_2C_6H_5)_2]_3$ (2g). $(NPCl_2)_3$ (2.30×10^{-2} mol) in dioxane (25 ml) was added slowly to a stirred solution of sodium 4-benzyloxybenzyloxide (2.02×10^{-2} mol) in dioxane (125 ml) at room temperature. After the mixture had been stirred for 17 h, the solvent was removed by a rotary evaporation. The product was purified by column chromatography using a dichloromethane/hexane mixture as the eluent.

Synthesis of $[NP(OC_6H_4OC_6H_5)_2]_4$ (4a). A solution of $(NPCl_2)_4$ (4.3×10^{-3} mol) in dioxane (30 ml) was added to a stirred solution of sodium 4-phenoxyphenoxide (6.9×10^{-2} mol) in dioxane (75 ml) at room temperature. The reaction mixture was refluxed for 24 h and was then cooled to room temperature, and the solvent was removed. The product was dissolved in dichloromethane and was filtered through silica gel. The dichloromethane was removed and the residue was dissolved in toluene and extracted with aqueous 1M NaOH. The toluene was removed and the product was purified by column chromatography using a dichloromethane/hexane mixture as the eluent.

Synthesis of $OP(O\text{-}C_6H_4\text{-}^tBu)_2NP(O\text{-}C_6H_4\text{-}^tBu)_3$ (6a). A solution of OP_2NPCl_5 (7.4×10^{-2} mol) in dioxane (100 ml) was treated with a solution of sodium 4-t-butylphenoxide (7.4×10^{-2} mol) in dioxane (100 ml). The reaction mixture was stirred at room temperature for 3 h . After filtration and reduction of the solvent volume, the crude product was chromatographed through a silica gel column using a dichloromethane/hexane mixture as eluent. The product was recrystallized from hexane by slow evaporation.

General Synthesis of High Polymers. The following procedure is a typical synthesis of the polymers discussed in this paper. **Synthesis of $[NP(OC_6H_4O\text{-}C_6H_5)_2]_n$.** A solution of $(NPCl_2)_n$ (3.0g, 5.3×10^{-2} mol) in dioxane (250 ml) and a solution of sodium-4-phenoxyphenoxide [prepared from Na (5.59g, 2.43×10^{-1} mol) and 4-phenoxyphenol (47.28g, 2.45×10^{-1} mol) in dioxane (300 ml)], were placed in an autoclave reaction vessel. The mixture was heated to 150 °C for 40h, then cooled to room temperature. The reaction mixture was concentrated, and the polymer was recovered by precipitation into water. The reaction product was soluble in THF and was purified by repeated precipitations into water and hexane from a THF solution. The polymer was further purified by Soxhlet extraction against methanol (72h) and hexane (72h). The polymer was dried under vacuum.

X-ray Structure Determination Techniques. Our general x-ray structural technique has been described in earlier papers[31,32] and only the details related to the present work will be given here. The structures were solved by direct methods using MULTAN'82.[28] In each case, the first E-map revealed the position of all non-hydrogen atoms. In **2a**, **2b**, **2e**, **2f** and **5a** all the non hydrogen atoms were refined anisotropically. In structures **2f** and **4a**, due to available memory, starred C atoms were refined isotropically. Difference Fourier syntheses calculated towards the end of the refinements, showed maxima consistent with the expected positions of hydrogen atoms in all the structures. In **2a**, **2b**, **2e**, **2f** and **6a** hydrogen atoms were included at geometrically idealized positions and at overall isotropic temperature factors. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann[33] and those from hydrogen atoms from Stewart and Davidson[34]. At the conclusion of the refinements, the values R and R_w were 0.0851 and 0.1129 (**2a**); 0.0500 and 0.0500 (**2b**); 0.0348 and 0.0447 (**2e**); 0.1181 and 0.1181 (**2f**); 0.0992 and 0.0992 (**4a**) and 0.0918 and 0.1066 (**6a**);

Acknowledgment: We thank the Office of Naval Research for support of this work. We also thank M. N. Mang for his suggestions.

Additional material available from the Cambridge Crystallographic Centre comprises positional parameters, bond distances, bond angles, general thermal parameters, and structure factor tables.

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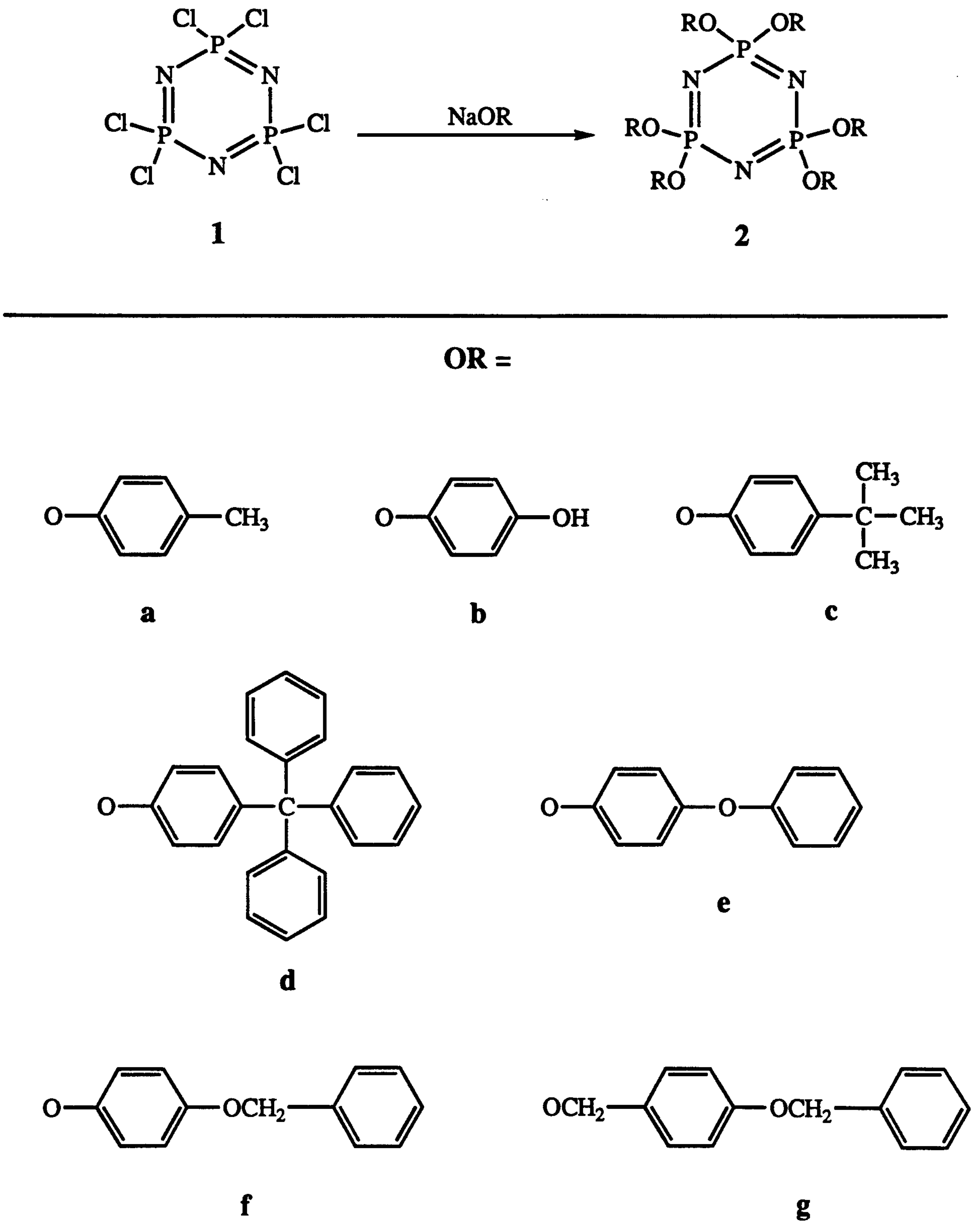
Scheme 1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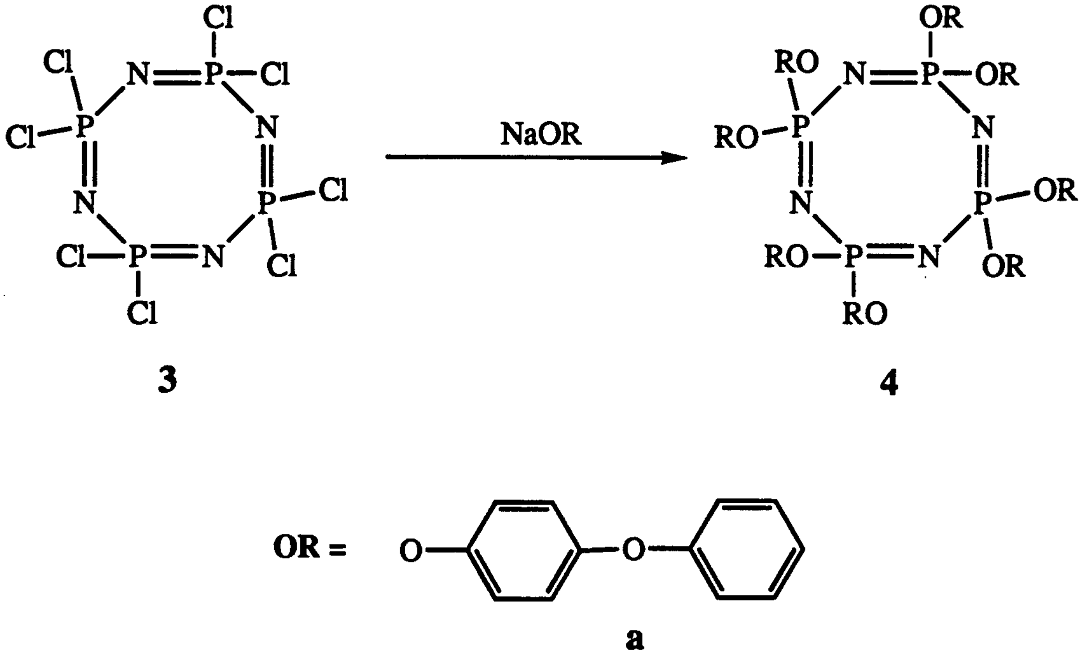
N
Cl
P
P
Cl
Cl
N
Cl
1
NaOR
RO
OR
P
N
N
RO
P
P
OR
RO
N
OR
2
OR =
O
CH3
a
O
OH
b
O
CH3
C
CH3
CH3
c
O
C
d
O
O
e
O
OCH2
f
OCH2
OCH2
g

Scheme 2



Scheme 3

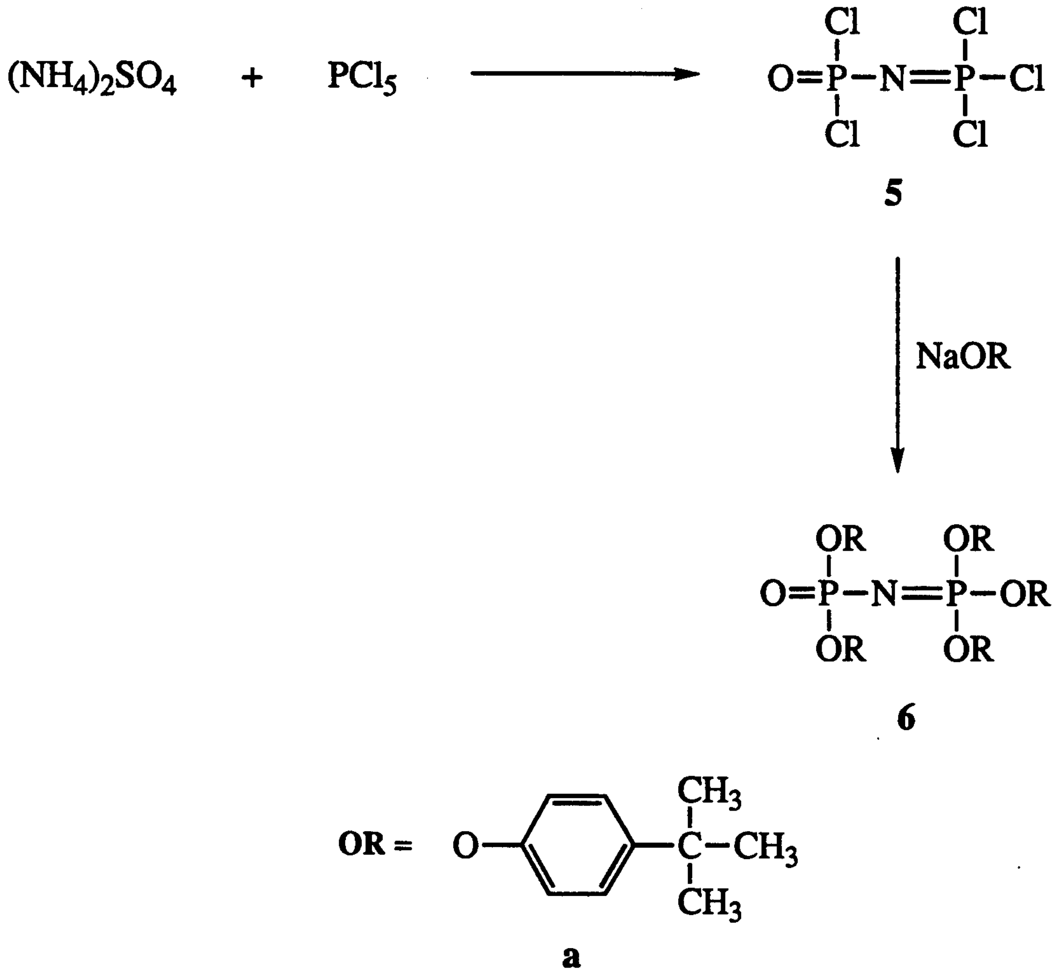

(NH4)2SO4
+
PCl5
Cl Cl
O=P−N=P−Cl
Cl Cl
5
NaOR
OR OR
O=P−N=P−OR
OR OR
6
OR =
O
CH3
C−CH3
CH3
a

Table 1. Characterization Data

Compound	Mp (°C)	Mass Spectral Data		Elemental Analysis Data		^{31}P NMR Chemical Shifts
		Found	Calculated	Found	Calculated	$P(OR)_2$ (ppm)
2a	116-117	777	777	C 64.79[a]	64.86	9.2
				H 5.50	5.41	
				N 5.40	5.41	
2b	241-243	789	789	C 54.60[b]	54.76	8.0
				H 3.90	3.80	
				N 5.20	5.32	
2c	#	1029	1029	#		8.7
2d	144*	unresolved	2145	C 83.27	83.89	8.6
				H 5.54	5.35	
				N 2.90	1.96	
2e	201-202	1149	1149	C 75.55	75.20	9.3
				H 4.66	4.70	
				N 3.68	3.66	
2f	100-101	1245	1245	C 69.57	69.40	9.3
				H 4.63	4.34	
				N 3.20	3.37	

2g	125-127	1413	1413	C 71.82 H 5.22 N 3.04	70.42 5.00 3.16	9.8
4a	68	1661	1661	C 68.64 H 4.12 N 3.38	69.39 4.37 3.37	-11.8
6a	85-87	837	856 (6a + H_20)	#		-22.24 ($P(OR)_3$) -15.99 ($P(OR)_2$)

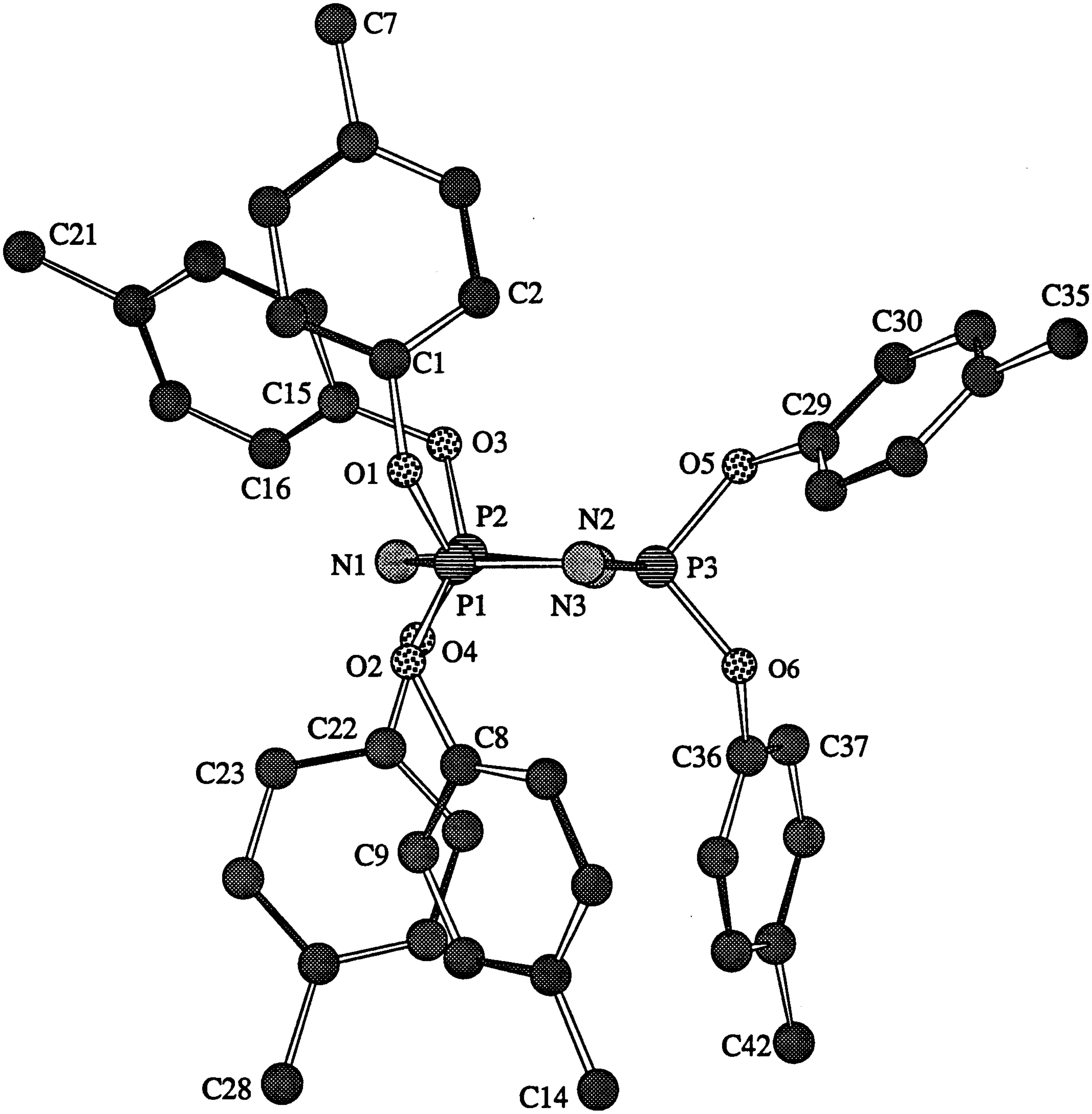
a: Reference 29
b: Reference 30
*: Decomposition
#: Data not obtained

Table 2. Summary of Crystal Data and Intensity Collection Parameters

	2a	2b	2e
Formula	$C_{42}H_{42}N_3P_3O_6$	$C_{36}H_{30}N_3P_3O_{12} \cdot 3H_2O$	$C_{72}H_{54}N_3P_3O_6$
Fw, amu	777	789	1149
Space group	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
Cryst. system	Triclinic	Triclinic	Triclinic
a, Å	9.791(2)	9.577(5)	15.348(6)
b, Å	11.399(4)	10.147(2)	15.567(5)
c, Å	18.495(3)	20.395(6)	16.035(3)
α, deg	97.86(2)	77.65(2)	77.02(2)
β, deg	95.33(1)	85.45(3)	66.55(3)
γ, deg	102.85(2)	84.03(2)	59.87(4)
V, $Å^3$	1977.2	1922.5	3038.2
Z	2	2	2
d(cald), g/cm^3	1.306	(cal) 1.363; (obs) 1.457	1.36
μ, cm^{-1}	1.79	2.2	1.604
Radiation (λ, Å)	CuKα; 1.5418	CuKα; 1.5418	CuKα; 1.5418
T, K	293	293	293
R, $R_w = (\Sigma\Delta^2/\Sigma wFo^2)^{1/2}$	0.085, 0.112	0.050, 0.050	0.076, 0.095

Table 2. **Summary of Crystal Data and Intensity Collection Parameters (cont)**

	2f	**4a**	**6a**
Formula	$C_{78}H_{66}N_3P_3O_{12}$	$C_{96}H_{72}N_4P_4O_{16}$	$C_{50}H_{65}NO_6P_2 \cdot H_2O$
Fw, amu	1329	1660	856
Space group	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
Cryst. system	Triclinic	Triclinic	Triclinic
a, Å	9.297(5)	16.728(1)	13.058(5)
b, Å	15.551(4)	20.516(9)	14.467(2)
c, Å	23.342(4)	25.760(2)	14.840(11)
α, deg	84.12(2)	106.04(3)	70.07(3)
β, deg	89.44(3)	93.551(6)	84.38(4)
γ, deg	80.55(2)	101.33(1)	74.55(3)
V, $Å^3$	3311.3	8266.9	2540.2
Z	2	4 (2 x 2 conformations)	2
d(cald), g/cm^3	1.33	(cal) 0.667 (obs) 1.33	1.12
μ, cm^{-1}	12.79	13.36	1.06
Radiation (λ, Å)	CuKα; 1.5418	CuKα; 1.5418	CuKα; 1.5418
T, K	293	293	293
R, $R_w = (\Sigma\Delta^2/\Sigma wFo^2)^{1/2}$	0.1187, 0.1187	0.0992, 0.0992	0.0918, 0.1066


C7
C21
C2
C35
C30
C1
C15
C29
O3
O1
O5
C16
P2
N2
N1
P3
P1
N3
O4
O2
O6
C22
C8
C36
C37
C23
C9
C42
C28
C14

2a

Figure 1

Table 3. Bond Distances (Å) and Bond Angles (deg) for 2a.

P1-O1	1.584(3)	O1-C1	1.425(5)
P1-O2	1.595(3)	O2-C8	1.402(5)
P1-N1	1.570(3)	O3-C15	1.399(6)
P1-N3	1.583(4)	O4-C22	1.416(5)
P2-O3	1.583(4)	O5-C29	1.376(5)
P2-O4	1.584(2)	O6-C36	1.385(5)
P2-N1	1.589(4)	C4-C7	1.521(7)
P2-N2	1.568(4)	C11-C14	1.514(8)
P3-O5	1.583(3)	C18-C21	1.497(7)
P3-O6	1.575(4)	C25-C28	1.530(7)
P3-N2	1.570(4)	C32-C35	1.489(8)
P3-N3	1.566(4)	C39-C42	1.489(7)

O1-P1-O2	94.5(1)	P2-O4-C22	124.1(3)
O1-P1-N1	110.2(2)	P3-O5-C29	127.4(3)
O1-P1-N3	111.7(2)	P3-O6-C36	126.7(4)
O2-P1-N1	110.9(2)	P1-N1-P2	122.0(2)
O2-P1-N3	110.6(2)	P2-N2-P3	122.0(2)
N1-P1-N3	116.9(2)	P1-N3-P3	123.7(2)
O3-P2-O4	99.3(2)	O1-C1-C2	117.0(4)
O3-P2-N1	112.6(2)	O1-C1-C6	120.4(4)
O3-P2-N2	106.0(2)	C3-C4-C7	119.1(4)
O4-P2-N1	109.3(2)	C5-C4-C7	121.8(5)
O4-P2-N2	110.5(2)	O2-C8-C9	118.9(4)
N1-P2-N2	117.6(2)	O2-C8-C13	119.1(3)
O5-P3-O6	100.5(2)	C10-C11-C14	120.4(4)
O5-P3-N2	107.6(2)	C12-C11-C14	121.0(4)
O5-P3-N3	109.7(2)	O3-C15-C16	121.3(3)
O6-P3-N2	111.7(2)	O3-C15-C20	118.2(3)
O6-P3-N3	108.9(3)	C17-C18-C21	121.6(3)
N2-P3-N3	117.2(2)	C19-C18-C21	121.3(3)
P1-O1-C1	123.5(2)	O4-C22-C23	118.6(4)
P1-O2-C8	122.9(3)	O4-C22-C27	119.4(4)
P2-O3-C15	123.3(3)	C24-C25-C28	121.4(5)

Table 3. Bond Distances (Å) and Bond Angles (deg) for 2a (cont).

C26-C25-C28	120.3(4)	O6-C36-C37	120.4(4)
O5-C29-C30	115.7(4)	O6-C36-C41	118.4(4)
O5-C29-C34	124.7(4)	C38-C39-C42	120.3(5)
C31-C32-C35	121.6(5)	C40-C39-C42	123.2(5)
C33-C32-C35	121.9(5)		

Numbers in parentheses are estimated standard deviations in the least significant digits. Phenoxy ring carbons are set to a C-C bond distance of 1.395 Å and a C-C-C bond angle of 120.0°in the x-ray crystal refinement program.

Table 4. Positional Parameters (Å) for 2a.

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
P1	0.0807(1)	0.85067(9)	0.83098(6)	4.10(2)
P2	-0.1612(1)	0.8914(1)	0.75981(6)	4.40(2)
P3	0.0628(1)	0.8726(1)	0.68385(6)	4.69(3)
O1	0.1797(3)	0.9403(2)	0.8980(2)	4.69(7)
O2	0.0978(3)	0.7301(2)	0.8618(2)	4.82(7)
O3	-0.1984(3)	1.0203(2)	0.7724(2)	4.68(6)
O4	-0.3160(3)	0.8063(3)	0.7477(2)	5.53(8)
O5	0.1459(3)	0.9877(3)	0.6536(2)	5.99(7)
O6	0.0730(3)	0.7671(3)	0.6215(2)	8.1(1)
N1	-0.0750(3)	0.8652(3)	0.8305(2)	4.11(8)
N2	-0.0935(3)	0.8844(3)	0.6863(2)	5.23(9)
N3	0.1462(3)	0.8585(3)	0.7573(2)	4.83(8)
C1	0.1798(4)	1.0660(4)	0.9155(2)	4.11(9)
C2	0.1565(4)	1.1057(4)	0.9846(2)	4.8(1)
C3	0.1627(4)	1.2294(4)	1.0052(3)	5.0(1)
C4	0.1944(4)	1.3097(4)	0.9561(3)	5.0(1)
C5	0.2200(4)	1.2664(4)	0.8879(3)	5.2(1)
C6	0.2145(4)	1.1431(4)	0.8660(2)	4.7(1)

Table 4. Positional Parameters (Å) for 2a (cont).

Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A2)
C7	0.1954(6)	1.4432(5)	0.9792(3)	7.4(2)
C8	0.0879(4)	0.6191(3)	0.8159(2)	4.22(9)
C9	-0.0337(4)	0.5298(4)	0.8084(3)	5.1(1)
C10	-0.0381(5)	0.4160(4)	0.7690(3)	5.8(1)
C11	0.0761(5)	0.3928(4)	0.7369(3)	5.4(1)
C12	0.1969(4)	0.4846(4)	0.7449(3)	5.4(1)
C13	0.2043(4)	0.5992(4)	0.7855(3)	4.9(1)
C14	0.0691(6)	0.2677(5)	0.6945(3)	7.8(2)
C15	-0.2548(4)	1.0633(4)	0.8347(2)	4.14(9)
C16	-0.3941(4)	1.0191(4)	0.8433(3)	5.0(1)
C17	-0.4469(4)	1.0689(4)	0.9024(3)	5.3(1)
C18	-0.3646(4)	1.1643(4)	0.9548(2)	4.6(1)
C19	-0.2255(4)	1.2064(4)	0.9448(3)	5.0(1)
C20	-0.1698(4)	1.1565(4)	0.8855(3)	4.6(1)
C21	-0.4248(5)	1.2200(5)	1.0188(3)	6.4(1)
C22	-0.3473(4)	0.6817(4)	0.7555(3)	4.7(1)
C23	-0.3890(4)	0.6508(5)	0.8198(3)	5.8(1)
C24	-0.4270(4)	0.5274(5)	0.8258(3)	6.0(1)

Table 4. Positional Parameters (Å) for 2a (cont).

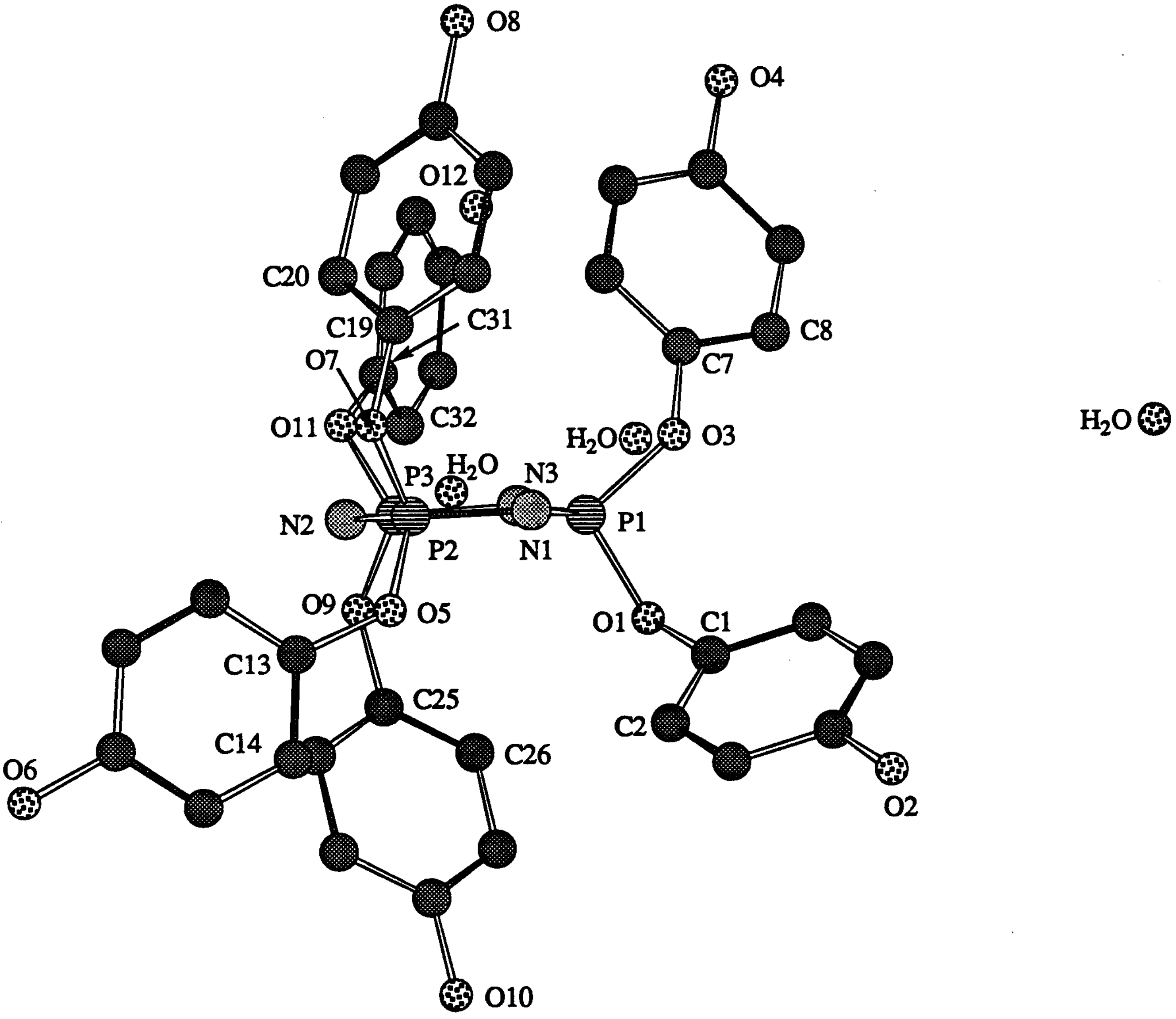
Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A2)
C25	-0.4203(4)	0.4390(4)	0.7699(3)	5.2(1)
C26	-0.3779(5)	0.4730(4)	0.7067(3)	5.5(1)
C27	-0.3409(4)	0.5957(4)	0.6976(3)	5.1(1)
C28	-0.4609(5)	0.3040(5)	0.7771(3)	7.8(2)
C29	0.2813(5)	1.0086(4)	0.6353(2)	5.4(1)
C30	0.3190(5)	1.1034(5)	0.5972(3)	7.0(1)
C31	0.4525(6)	1.1325(5)	0.5783(3)	7.7(1)
C32	0.5531(5)	1.0696(5)	0.5959(3)	6.6(1)
C33	0.5116(5)	0.9741(5)	0.6334(3)	6.2(1)
C34	0.3774(5)	0.9420(5)	0.6527(3)	6.1(1)
C35	0.6992(6)	1.1051(6)	0.5766(4)	9.1(2)
C36	-0.0382(4)	0.6779(4)	0.5816(3)	5.3(1)
C37	-0.1268(5)	0.7062(4)	0.5294(3)	6.4(1)
C38	-0.2279(5)	0.6151(5)	0.4868(3)	6.8(1)
C39	-0.2453(5)	0.4928(5)	0.4954(3)	6.1(1)
C40	-0.1562(5)	0.4689(4)	0.5494(3)	6.2(1)
C41	-0.0502(5)	0.5607(4)	0.5926(3)	6.1(1)
C42	-0.3557(7)	0.3961(6)	0.4464(4)	10.3(2)

The form of the anisotropic thermal parameter is:

$$U = \exp[-2\pi^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3)$$

$$+ 2klbcU(2,3))\}]$$ where a, b, and c are reciprocal lattice constants


O8
O4
O12
C20
C19
C31
O7
C8
C7
O11
C32
H_2O
O3
H_2O
P3
H_2O
N3
N2
P2
N1
P1
O9
O5
O1
C1
C13
C25
C2
O6
C14
C26
O2
O10

2b

Figure 2

Table 5. Bond Distances (Å) and Bond Angles (deg) for 2b.

P1-O1	1.565(2)	O1-C1	1.400(4)
P1-O3	1.586(2)	O2-C4	1.386(4)
P1-N1	1.574(3)	O3-C7	1.399(4)
P1-N3	1.584(3)	O4-C10	1.357(4)
P2-O5	1.574(2)	O5-C13	1.409(5)
P2-O7	1.562(3)	O6-C16	1.378(4)
P2-N1	1.572(3)	O7-C19	1.393(3)
P2-N2	1.581(3)	O8-C22	1.377(4)
P3-O9	1.577(2)	O9-C25	1.417(3)
P3-O11	1.572(2)	O10-C28	1.383(4)
P3-N2	1.585(3)	O11-C31	1.404(3)
P3-N3	1.579(2)	O12-C34	1.382(4)

O1-P1-O3	100.7(1)	P3-O9-C25	116.7(2)
O1-P1-N1	105.7(1)	P3-O11-C31	126.5(3)
O1-P1-N3	113.4(1)	P1-N1-P2	122.8(2)
O3-P1-N1	109.7(1)	P2-N2-P3	121.1(2)
O3-P1-N3	110.0(1)	P1-N3-P3	123.7(2)
N1-P1-N3	116.2(1)	O1-C1-C2	117.0(3)
O5-P2-O7	101.5(1)	O1-C1-C6	122.8(3)
O5-P2-N1	110.6(1)	O2-C4-C3	118.3(3)
O5-P2-N2	106.1(1)	O2-C4-C5	121.7(4)
O7-P2-N1	107.6(1)	O3-C7-C8	120.9(3)
O7-P2-N2	111.8(1)	O3-C7-C12	118.9(4)
N1-P2-N2	118.1(1)	O4-C10-C9	117.0(3)
O9-P3-O11	100.6(1)	O4-C10-C11	123.3(4)
O9-P3-N2	109.9(1)	O5-C13-C14	118.8(3)
O9-P3-N3	109.8(1)	O5-C13-C18	118.8(3)
O11-P3-N2	111.1(1)	O6-C16-C15	117.3(3)
O11-P3-N3	107.0(1)	O6-C16-C17	121.3(3)
N2-P3-N3	117.1(1)	O7-C19-C20	121.5(3)
P1-O1-C1	129.3(3)	O7-C19-C24	116.7(3)
P1-O3-C7	118.6(2)	O8-C22-C21	119.1(3)
P2-O5-C13	121.0(2)	O8-C22-C23	120.0(4)
P2-O7-C19	127.1(2)	O9-C25-C26	119.4(3)

Table 5. Bond Distances (Å) and Bond Angles (deg) for 2b (cont).

O9-C25-C30	119.1(3)	O11-C31-C36	120.0(3)
O10-C28-C27	120.7(3)	O12-C34-C33	122.3(3)
O10-C28-C29	118.7(3)	O12-C34-C35	118.3(4)
O11-C31-C32	122.7(3)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

Phenoxy ring carbons are set to a C-C bond distance of 1.395 Å and a C-C-C bond angle of 120.0°in the x-ray crystal refinement program.

Table 6. Positional Parameters (Å) for 2b.

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
P1	0.89125(8)	0.18930(9)	0.19387(4)	3.23(2)
P2	0.63708(8)	0.08822(8)	0.24112(4)	3.03(2)
P3	0.77387(9)	0.21602(9)	0.32041(4)	3.07(2)
01	0.8963(2)	0.3045(2)	0.1292(1)	3.91(5)
02	1.2109(3)	0.7461(3)	0.0583(1)	5.37(7)
03	1.0347(2)	0.1016(2)	0.1826(1)	3.80(5)
04	1.1398(3)	-0.4058(3)	0.3428(1)	5.95(7)
05	0.4938(2)	0.1698(2)	0.2120(1)	3.92(5)
06	0.3438(3)	0.1661(2)	-0.0420(1)	4.73(6)
07	0.5993(3)	-0.0610(2)	0.2507(1)	5.04(6)
08	0.6358(4)	-0.4761(3)	0.4721(2)	8.09(9)
09	0.7092(2)	0.3548(2)	0.3377(1)	3.52(5)
010	0.4494(3)	0.7273(3)	0.1350(1)	4.91(6)
011	0.8511(2)	0.1508(2)	0.3864(1)	3.95(5)
012	0.6427(3)	-0.1572(3)	0.6240(1)	5.90(7)
OW13	0.1414(3)	0.3637(3)	0.2986(2)	7.03(8)
OW14	0.2017(3)	0.9717(3)	0.9430(1)	6.15(7)
OW15	0.1118(6)	0.5664(6)	0.4797(3)	16.7(2)
N1	0.7637(3)	0.1080(3)	0.1870(1)	3.56(6)

Table 6 Positional Parameters (Å) for 2b (cont).

Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A2)
N2	0.6518(3)	0.1290(3)	0.3107(1)	3.20(6)
N3	0.8913(3)	0.2426(3)	0.2614(1)	3.18(6)
C1	0.9808(3)	0.4128(3)	0.1128(2)	3.40(7)
C2	0.9186(4)	0.5358(4)	0.0810(2)	4.33(9)
C3	0.9969(4)	0.6465(4)	0.0625(2)	4.50(9)
C4	1.1364(4)	0.6324(4)	0.0755(2)	3.92(8)
C5	1.1982(4)	0.5090(4)	0.1051(2)	4.48(9)
C6	1.1223(4)	0.3983(4)	0.1238(2)	4.28(9)
C7	1.0583(3)	-0.0268(3)	0.2238(2)	3.63(8)
C8	1.1008(3)	-0.0415(4)	0.2884(2)	4.19(8)
C9	1.1266(4)	-0.1695(4)	0.3279(2)	4.46(9)
C10	1.1117(4)	-0.2830(4)	0.3019(2)	4.49(9)
C11	1.0710(4)	-0.2670(4)	0.2368(2)	4.43(9)
C12	1.0434(4)	-0.1397(4)	0.1981(2)	4.20(8)
C13	0.4606(3)	0.1667(3)	0.1471(2)	3.43(7)
C14	0.4991(4)	0.2665(3)	0.0945(2)	4.00(8)
C15	0.4584(4)	0.2672(4)	0.0306(2)	4.20(8)
C16	0.3801(3)	0.1646(3)	0.0222(2)	3.67(8)
C17	0.3413(3)	0.0657(4)	0.0753(2)	3.97(8)

Table 6. Positional Parameters (Å) for 2b (cont).

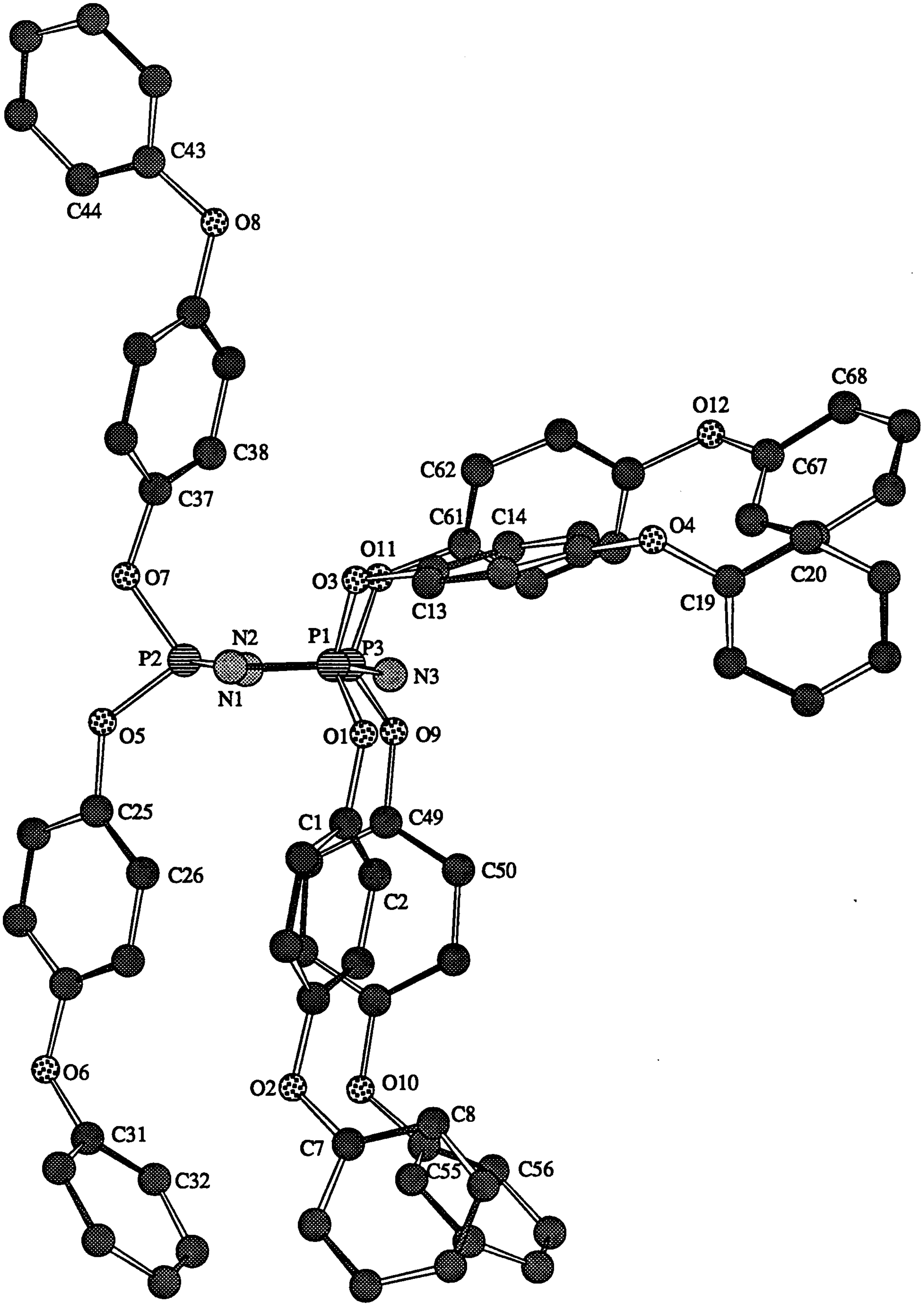
Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A2)
C18	0.3808(3)	0.0657(4)	0.1394(2)	3.88(8)
C19	0.6119(3)	-0.1627(3)	0.3084(2)	3.31(7)
C20	0.7374(4)	-0.1979(4)	0.3389(2)	4.48(9)
C21	0.7444(4)	-0.3026(4)	0.3938(2)	5.3(1)
C22	0.6278(5)	-0.3705(4)	0.4172(2)	5.2(1)
C23	0.5023(4)	-0.3346(4)	0.3847(2)	5.00(9)
C24	0.4968(3)	-0.2308(4)	0.3305(2)	4.16(8)
C25	0.6434(3)	0.4498(3)	0.2854(2)	3.23(7)
C26	0.7207(3)	0.5422(3)	0.2440(2)	3.74(8)
C27	0.6575(4)	0.6368(3)	0.1934(2)	3.84(8)
C28	0.5160(4)	0.6349(3)	0.1854(2)	3.59(8)
C29	0.4389(3)	0.5425(4)	0.2274(2)	4.11(8)
C30	0.5008(3)	0.4480(4)	0.2786(2)	3.89(8)
C31	0.7910(3)	0.0758(3)	0.4459(2)	3.45(7)
C32	0.6755(4)	0.1262(4)	0.4807(2)	4.52(9)
C33	0.6245(4)	0.0484(4)	0.5396(2)	4.65(9)
C34	0.6895(4)	-0.0764(4)	0.5646(2)	4.21(8)
C35	0.8050(4)	-0.1238(4)	0.5304(2)	5.4(1)
C36	0.8549(4)	-0.0483(4)	0.4706(2)	4.9(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$

Where a, b, and c are reciprocal lattice constants.


C43
C44
O8
C38
C37
O7
P2
N2
N1
P1
P3
N3
O3
O11
C61
C14
C62
O12
C68
C67
O4
C20
C19
C13
O5
O1
O9
C25
C1
C49
C26
C50
C2
O6
O2
O10
C8
C7
C31
C55
C56
C32

2e

Figure 3

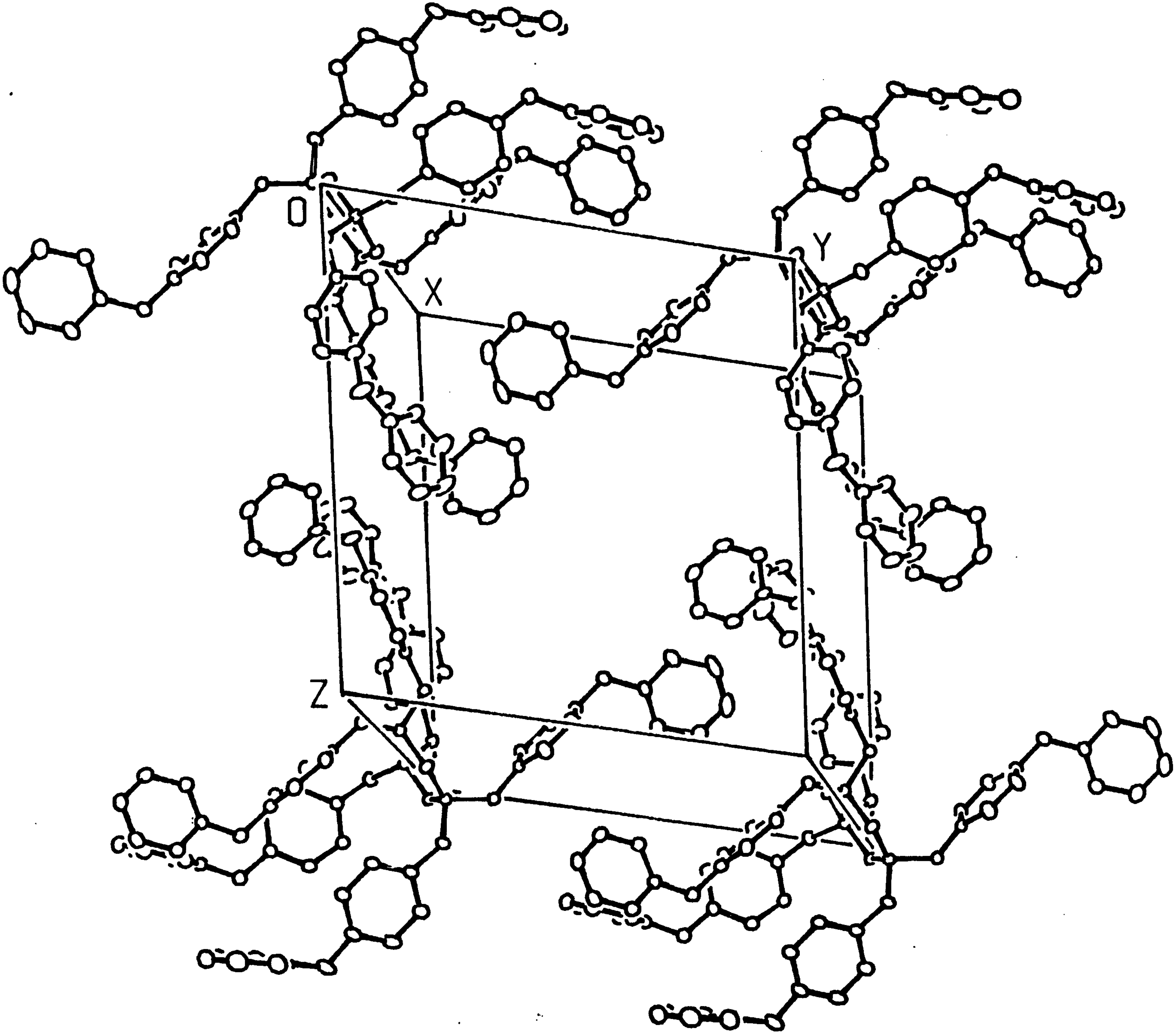


Figure 4

Table 7. Bond Distances (Å) and Bond Angles (deg) for 2e

P1-O1	1.583(2)	O3-C13	1.417(3)
P1-O3	1.582(1)	O4-C16	1.394(3)
P1-N1	1.574(2)	O4-C19	1.375(2)
P1-N3	1.569(2)	O5-C25	1.400(2)
P2-O5	1.565(1)	O6-C28	1.381(3)
P2-O7	1.577(1)	O6-C31	1.394(4)
P2-N1	1.582(2)	O7-C37	1.403(2)
P2-N2	1.572(2)	O8-C40	1.395(3)
P3-O9	1.583(1)	O8-C43	1.389(3)
P3-O11	1.579(2)	O9-C49	1.410(2)
P3-N2	1.574(2)	O10-C52	1.379(3)
P3-N3	1.583(2)	O10-C55	1.395(3)
O1-C1	1.407(2)	O11-C61	1.407(2)
O2-C4	1.397(3)	O12-C64	1.393(3)
O2-C7	1.381(3)	O12-C67	1.380(4)

O1-P1-O3	98.39(9)	C4-O2-C7	118.6(2)
O1-P1-N1	111.04(9)	P1-O3-C13	122.6(1)
O1-P1-N3	109.90(9)	C16-O4-C19	117.1(2)
O3-P1-N1	106.97(7)	P2-O5-C25	131.2(1)
O3-P1-N3	112.12(8)	C28-O6-C31	120.0(2)
N1-P1-N3	116.8(1)	P2-O7-C37	126.4(1)
O5-P2-O7	93.16(7)	C40-O8-C43	117.7(2)
O5-P2-N1	111.0(1)	P3-O9-C49	123.5(1)
O5-P2-N2	111.91(9)	C52-O10-C55	120.1(2)
O7-P2-N1	110.80(9)	P3-O11-C61	122.8(2)
O7-P2-N2	111.4(1)	C64-O12-C67	118.9(2)
N1-P2-N2	116.27(9)	P1-N1-P2	122.9(1)
O9-P3-O11	98.86(7)	P2-N2-P3	122.3(1)
O9-P3-N2	107.44(9)	P1-N3-P3	121.8(1)
O9-P3-N3	111.20(9)	O1-C1-C2	121.3(2)
O11-P3-N2	107.44(9)	O1-C1-C6	117.4(2)
O11-P3-N3	111.20(9)	O2-C4-C3	120.3(2)
N2-P3-N3	117.0(1)	O2-C4-C5	119.6(2)
P1-O1-C1	125.5(2)	O2-C7-C8	123.2(3)

Table 7. Bond Distances (Å) and Bond Angles (deg) for 2e (cont).

O2-C7-C12	116.4(4)	O8-C40-C41	120.4(2)
O3-C13-C14	119.5(3)	O8-C43-C44	122.6(2)
O3-C13-C18	119.0(2)	O8-C43-C48	116.7(3)
O4-C16-C15	122.0(2)	O9-C49-C50	118.7(2)
O4-C16-C17	117.4(3)	O9-C49-C54	120.3(2)
O4-C19-C20	116.9(2)	O10-C52-C51	125.5(2)
O4-C19-C4	123.0(2)	O10-C52-C53	115.0(2)
O5-C25-C26	123.7(2)	O10-C55-C56	120.3(3)
O5-C25-C30	115.8(2)	O10-C55-C60	118.7(2)
O6-C28-C27	124.8(3)	O11-C61-C62	118.3(1)
O6-C28-C29	115.5(3)	O11-C61-C66	120.5(2)
O6-C31-C32	118.4(3)	O12-C64-C63	119.5(2)
O6-C31-C36	120.9(2)	O12-C64-C65	120.1(2)
O7-C37-C38	121.3(2)	O12-C67-C68	115.7(3)
O7-C37-C42	117.8(2)	O12-C67-C72	123.8(2)
O8-C40-C39	119.7(2)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

Phenoxy ring carbons are set to a C-C bond distance of 1.395 Å and a C-C-C bond angle of 120.0°in the x-ray crystal refinement program.

Table 8. Positional Parameters (Å) for 2e.

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
P1	0.27015(4)	0.02428(4)	0.06758(4)	3.02(2)
P2	0.30398(4)	-0.07887(4)	-0.07174(4)	3.05(2)
P3	0.09909(4)	0.05050(4)	0.02822(4)	3.04(2)
O1	0.3105(1)	0.1006(1)	0.0659(1)	3.54(4)
O2	0.3937(1)	0.3573(1)	-0.2177(1)	5.49(5)
O3	0.2920(1)	-0.0385(1)	0.1559(1)	3.52(4)
O4	0.2156(1)	0.1256(1)	0.4655(1)	6.64(6)
O5	0.3716(1)	-0.0830(1)	-0.1753(1)	4.00(5)
O6	0.3700(2)	0.1858(1)	-0.4662(1)	7.89(6)
O7	0.3431(1)	-0.1945(1)	-0.0623(1)	3.78(4)
O8	0.2642(1)	-0.4356(1)	0.2383(1)	5.21(5)
O9	0.0077(1)	0.1467(1)	0.0001(1)	3.65(4)
O10	0.0692(1)	0.4341(1)	-0.2550(1)	6.03(6)
O11	0.0293(1)	-0.0006(1)	0.0955(1)	3.44(4)
O12	-0.2428(1)	0.1161(1)	0.4456(1)	6.84(5)
N1	0.3466(1)	-0.0475(1)	-0.0147(1)	3.32(5)
N2	0.1804(1)	-0.0193(1)	-0.0548(1)	3.17(5)
N3	0.1478(1)	0.0811(1)	0.0801(1)	3.10(5)
C1	0.3290(1)	0.1659(1)	-0.0072(1)	3.11(6)
C2	0.2483(2)	0.2376(2)	-0.0377(2)	4.59(7)
C3	0.2702(2)	0.3024(2)	-0.1077(2)	5.03(7)
C4	0.3703(2)	0.2951(2)	-0.1445(2)	4.08(6)
C5	0.4497(2)	0.2240(2)	-0.1118(2)	4.44(7)
C6	0.4288(2)	0.1587(2)	-0.0430(2)	3.84(7)

Table 8. Positional Parameters (Å) for 2e (cont).

Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A2)
C7	0.3878(2)	0.4434(1)	-0.2002(1)	3.78(6)
C8	0.3323(2)	0.4858(2)	-0.1165(2)	4.41(7)
C9	0.3301(2)	0.5726(2)	-0.1066(2)	5.19(8)
C10	0.3811(2)	0.6165(2)	-0.1775(2)	5.54(8)
C11	0.4359(2)	0.5732(2)	-0.2602(2)	5.58(8)
C12	0.4390(2)	0.4870(2)	-0.2719(2)	4.81(7)
C13	0.2705(2)	0.0058(1)	0.2347(1)	3.25(6)
C14	0.1699(2)	0.0440(2)	0.2961(2)	4.28(7)
C15	0.1507(2)	0.0851(2)	0.3733(2)	5.10(8)
C16	0.2314(2)	0.0867(2)	0.3874(2)	4.61(7)
C17	0.3327(2)	0.0463(2)	0.3264(2)	4.47(7)
C18	0.3527(2)	0.0047(2)	0.2491(2)	3.94(7)
C19	0.1313(2)	0.2186(2)	0.4891(2)	4.70(7)
C20	0.0780(2)	0.2358(2)	0.5802(2)	5.31(8)
C21	-0.0054(2)	0.3281(2)	0.6070(2)	5.79(8)
C22	-0.0346(2)	0.4016(2)	0.5446(2)	5.98(8)
C23	0.0197(2)	0.3849(2)	0.4540(2)	5.79(8)
C24	0.1027(2)	0.2939(2)	0.4262(2)	5.25(8)
C25	0.3654(2)	-0.0080(2)	-0.2433(1)	3.49(6)
C26	0.3685(2)	0.0761(2)	-0.2368(1)	4.01(7)
C27	0.3705(2)	0.1433(2)	-0.3099(2)	4.43(7)
C28	0.3691(2)	0.1243(2)	-0.3893(2)	4.85(7)
C29	0.3660(2)	0.0399(2)	-0.3949(2)	6.26(8)
C30	0.3655(2)	-0.0275(2)	-0.3229(2)	5.27(7)

Table 8. Positional Parameters (Å) for 2e (cont).

Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A2)
C31	0.3751(2)	0.2724(2)	-0.4679(2)	5.35(8)
C32	0.2842(2)	0.3594(2)	-0.4567(2)	6.8(1)
C33	0.2890(3)	0.4458(2)	-0.4640(2)	7.6(1)
C34	0.3832(2)	0.4456(2)	-0.4820(2)	7.6(1)
C35	0.4734(2)	0.3583(2)	-0.4924(2)	7.6(1)
C36	0.4688(2)	0.2711(2)	-0.4863(2)	6.7(1)
C37	0.3193(2)	-0.2490(1)	0.0184(1)	3.19(6)
C38	0.2179(2)	-0.2353(2)	0.0650(2)	3.92(7)
C39	0.2002(2)	-0.2986(2)	0.1389(2)	4.43(7)
C40	0.2835(2)	-0.3735(2)	0.1634(1)	3.83(7)
C41	0.3846(2)	-0.3856(2)	0.1168(2)	5.23(8)
C42	0.4023(2)	-0.3225(2)	0.0439(2)	4.88(8)
C43	0.2992(2)	-0.5336(2)	0.2220(2)	4.08(7)
C44	0.3064(2)	-0.5612(2)	0.1440(2)	5.40(8)
C45	0.3377(2)	-0.6595(2)	0.1341(2)	6.47(9)
C46	0.3623(2)	-0.7277(2)	0.1996(3)	7.8(1)
C47	0.3553(2)	-0.7001(2)	0.2780(2)	7.8(1)
C48	0.3229(2)	-0.6020(2)	0.2900(2)	5.82(9)
C49	0.0264(1)	0.2197(1)	-0.0634(1)	3.18(6)
C50	-0.0175(2)	0.3129(2)	-0.0345(1)	3.77(7)
C51	-0.0060(2)	0.3878(2)	-0.0959(2)	4.21(7)
C52	0.0512(2)	0.3669(2)	-0.1867(2)	3.98(7)
C53	0.0949(2)	0.2723(2)	-0.2147(1)	3.97(7)
C54	0.0826(2)	0.1981(2)	-0.1540(1)	3.69(6)

Table 8. Positional Parameters (Å) for 2e (cont).

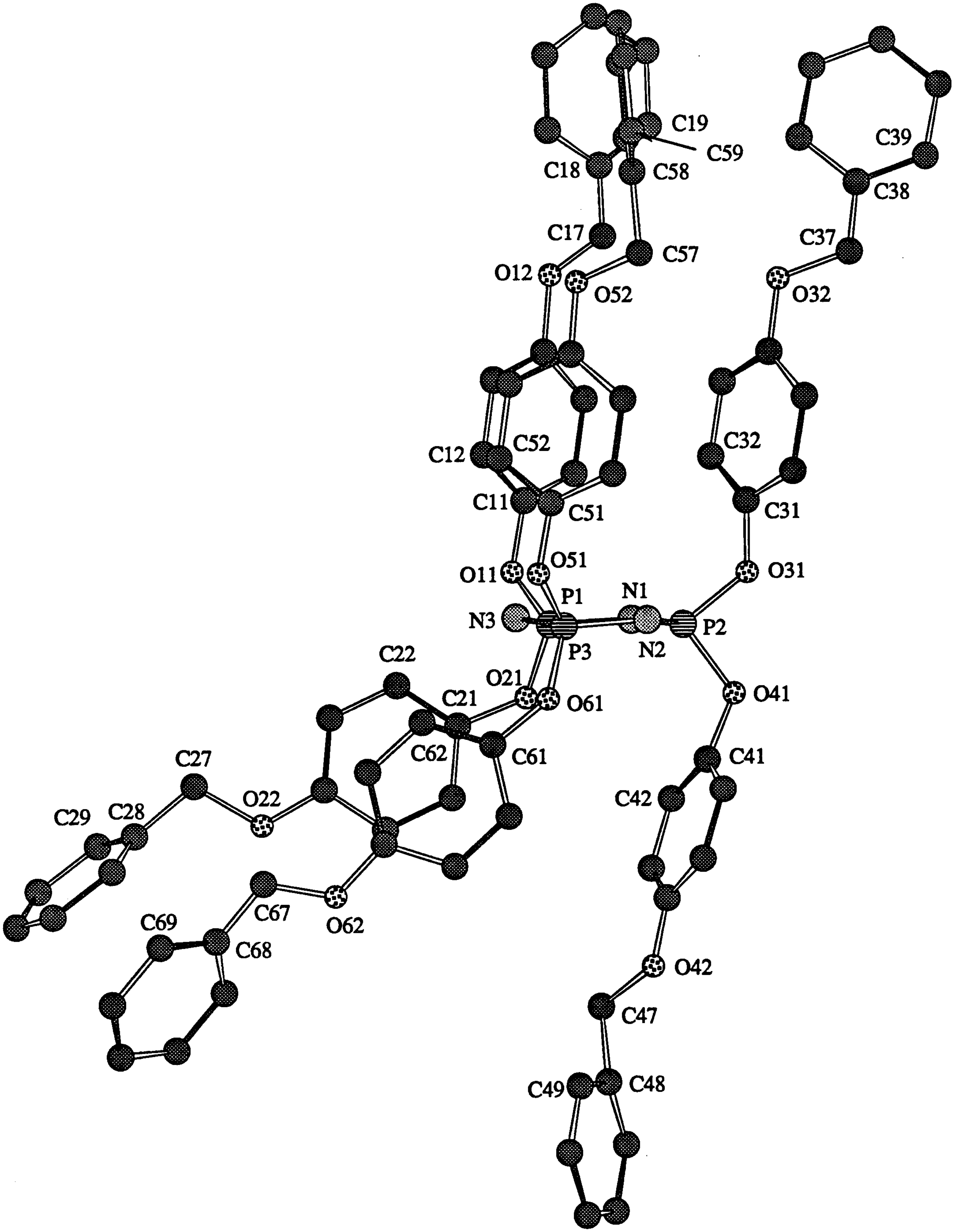
Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A2)
C55	0.0483(2)	0.5260(2)	-0.2332(2)	4.48(7)
C56	-0.0535(2)	0.6029(2)	-0.2121(2)	5.51(8)
C57	-0.0689(2)	0.6950(2)	-0.1991(2)	6.3(1)
C58	0.0147(2)	0.7087(2)	-0.2073(2)	6.06(9)
C59	0.1144(2)	0.6324(2)	-0.2290(2)	5.74(8)
C60	0.1319(2)	0.5401(2)	-0.2417(2)	4.90(8)
C61	-0.0392(1)	0.0326(1)	0.1839(1)	3.34(6)
C62	-0.0108(2)	-0.0256(2)	0.2561(2)	4.53(7)
C63	-0.0793(2)	0.0050(2)	0.3434(2)	5.45(8)
C64	-0.1723(2)	0.0902(2)	0.3572(2)	4.91(7)
C65	-0.2003(2)	0.1476(2)	0.2848(2)	4.94(8)
C66	-0.1337(2)	0.1181(2)	0.1972(2)	4.36(7)
C67	-0.2306(2)	0.1698(2)	0.4942(2)	4.43(7)
C68	-0.2957(2)	0.1839(2)	0.5837(2)	5.55(8)
C69	-0.2894(2)	0.2379(2)	0.6355(2)	7.0(1)
C70	-0.2199(2)	0.2764(2)	0.6006(2)	8.2(1)
C71	-0.1562(2)	0.2625(2)	0.5115(2)	7.7(1)
C72	-0.1610(2)	0.2085(2)	0.4580(2)	5.49(8)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$$4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$$

Where a, b, and c are reciprocal lattice constants.


C19
C59
C39
C18
C58
C38
C17
C37
C57
O12
O52
O32
C52
C32
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C11
C51
C31
O51
O11
O31
P1
N1
N3
P2
P3
N2
C22
O21
C21
O61
O41
C62
C61
C41
C27
O22
C42
C29
C28
C69
C67
O62
C68
O42
C47
C49
C48

2f

Figure 5

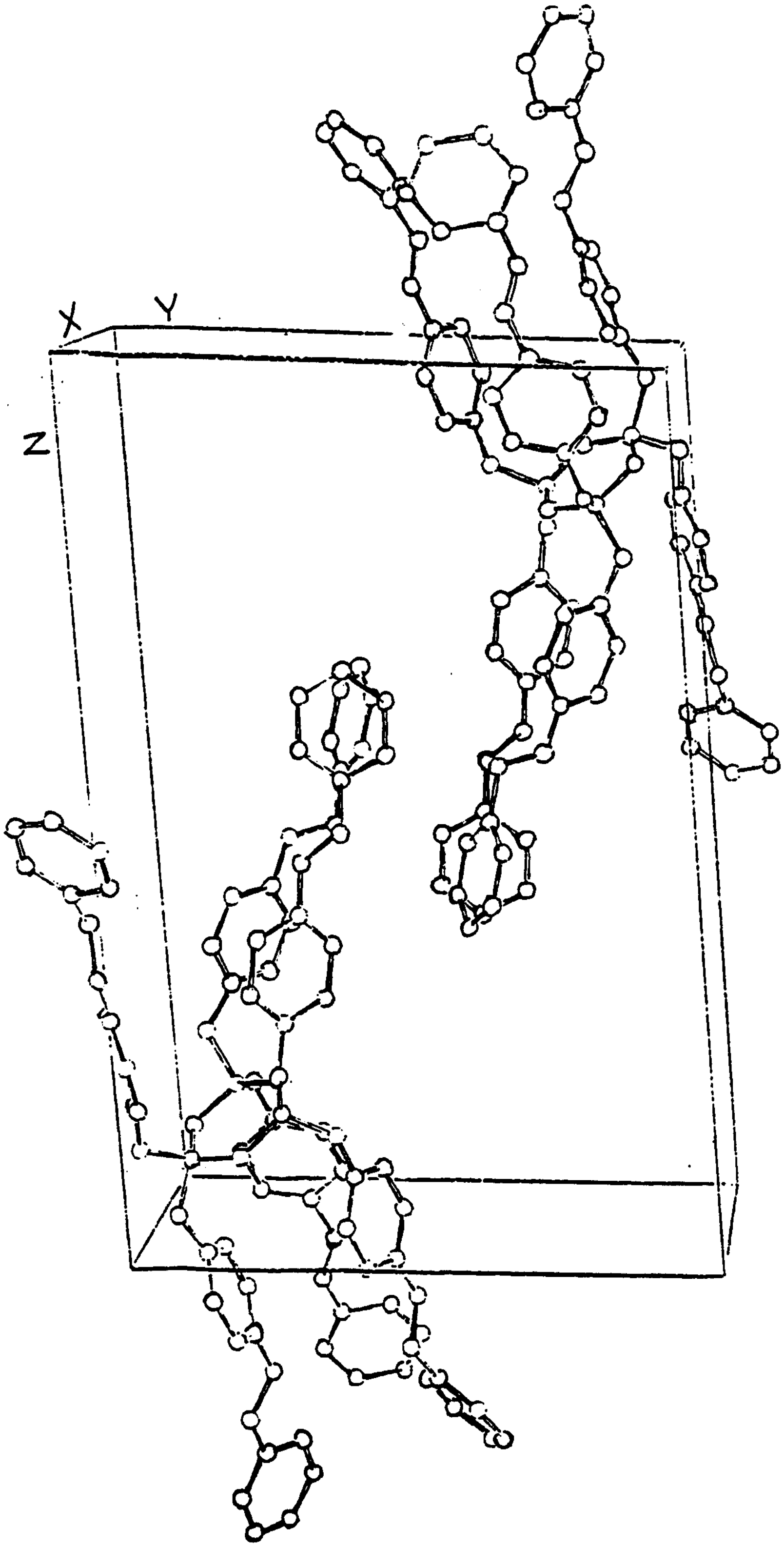


Figure 6

Table 9. Bond Distances (Å) and Bond Angles (deg) for 2f.

P1-N1	1.547(11)	O31-C31	1.375(13)
P1-N3	1.574(10)	O32-C34	1.377(10)
P1-O11	1.591(10)	O32-C37	1.424(11)
P1-O21	1.600(9)	O41-C41	1.380(11)
P2-N1	1.593(12)	O42-C44	1.353(12)
P2-N2	1.597(11)	O42-C47	1.635(9)
P2-O31	1.553(8)	O51-C51	1.587(10)
P2-O41	1.608(11)	O52-C54	1.352(14)
P3-N2	1.576(11)	O52-C57	1.436(11)
P3-N3	1.568(11)	O61-C61	1.373(10)
P3-O51	1.587(10)	O62-C64	1.344(9)
P3-O61	1.595(9)	O62-C67	1.369(9)
O11-C11	1.379(12)	C17-C18	1.352(11)
O12-C14	1.443(15)	C27-C28	1.462(6)
O12-C17	1.239(11)	C37-C38	1.347(8)
O21-C21	1.394(10)	C47-C48	1.640(8)
O22-C24	1.348(10)	C57-C58	1.562(10)
O22-C27	1.466(9)	C67-C68	1.396(6)

N1-P1-N3	119.2(6)	P1-N1-P2	121.6(7)
N1-P1-O11	109.9(5)	P2-N2-P3	120.1(7)
N3-P1-O11	110.9(6)	P1-N3-P3	119.7(7)
N1-P1-O21	106.6(6)	P1-O11-C11	124.5(7)
N3-P1-O21	110.4(5)	C14-O12-C17	130.6(14)
O11-P1-O21	97.7(5)	P1-O21-C21	124.3(7)
N1-P2-N2	117.1(6)	C24-O22-C27	119.3(7)
N1-P2-O31	112.6(6)	P2-O31-C31	128.2(8)
N2-P2-O31	110.6(5)	C34-O32-C37	117.6(7)
N1-P2-O41	110.8(6)	P2-O41-C41	120.1(7)
N2-P2-O41	110.4(6)	C44-O42-C47	112.6(7)
O31-P2-O41	92.7(5)	P3-O51-C51	120.0(7)
N2-P3-P3	119.3(6)	C54-O52-C57	114.6(10)
N2-P3-O51	108.8(5)	P3-O61-C61	127.8(7)
N3-P3-O51	110.2(6)	C64-O62-C67	122.8(8)
N2-P3-O61	107.2(6)	O11-C11-C12	120.2(7)
N3-P3-O61	112.0(5)	O11-C11-C16	119.7(8)
O51-P3-O61	97.1(5)	O12-C14-C13	120.0(7)

Table 9. Bond Distances (Å) and Bond Angles (deg) for 2f (cont).

O12-C14-C15	126.1(8)	O42-C44-C43	125.0(7)
O12-C17-C18	126.1(1)	O42-C44-C45	115.0(8)
O21-C21-C22	123.1(7)	O42-C47-C48	91.6(4)
O21-C21-C26	116.8(7)	O51-C51-C52	120.1(8)
O22-C24-C23	124.0(8)	O51-C51-C56	119.7(9)
O22-C24-C25	116.0(7)	O52-C54-C53	115.8(9)
O22-C27-C28	109.3(4)	O52-C54-C55	124.2(8)
O31-C31-C32	123.8(8)	O52-C57-C58	104.4(6)
O31-C31-C36	115.4(9)	O61-C61-C62	123.2(7)
O32-C34-C33	115.2(8)	O61-C61-C66	116.6(7)
O32-C34-C35	124.7(7)	O62-C64-C63	124.8(7)
O32-C37-C38	115.4(7)	O62-C64-C65	115.2(7)
O41-C41-C42	121.4(8)	O62-C67-C68	119.8(5)
O41-C41-C46	118.3(7)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

Phenoxy ring carbons are set to a C-C bond distance of 1.395 Å and a C-C-C bond angle of 120.0°in the x-ray crystal refinement program.

Table 10. Positional Parameters (Å) for 2f.

Atom	X	Y	Z	U(1,1)
P1	0.4459(4)	0.1579(2)	0.8317(1)	0.061(2)
P2	0.2392(5)	0.0945(2)	0.9009(1)	0.086(2)
P3	0.1790(4)	0.2573(2)	0.8399(1)	0.070(2)
N1	0.4009(12)	0.0870(7)	0.8765(4)	0.055(4)
N2	0.1335(12)	0.1860(7)	0.8864(4)	0.069(4)
N3	0.3414(11)	0.2484(7)	0.8195(4)	0.054(4)
O11	0.6075(10)	0.1721(6)	0.8448(4)	0.061(4)
O12	0.8023(14)	0.2756(11)	1.0496(4)	0.122(4)
O21	0.4793(10)	0.1130(5)	0.7732(3)	0.078(4)
O22	0.5851(10)	0.2705(6)	0.5573(3)	0.072(4)
O31	0.2356(11)	0.0637(6)	0.9662(3)	0.115(4)
O32	-0.4057(14)	-0.1842(8)	0.8347(4)	0.156(4)
O41	0.1627(11)	0.0152(6)	0.8837(4)	0.107(4)
O42	-0.0758(10)	-0.0027(7)	0.6709(4)	0.061(4)
O51	0.1271(11)	0.3514(6)	0.8607(4)	0.090(4)
O52	0.3166(13)	0.4534(8)	1.0625(4)	0.137(4)
O61	0.0679(10)	0.2672(6)	0.7871(4)	0.063(4)
O62	0.11324(10)	0.3291(6)	0.5529(3)	0.072(4)
C11	0.6528(9)	0.1954(5)	0.8963(3)	0.078(4)
C12	0.6417(9)	0.2836(5)	0.9053(3)	0.064(4)
C13	0.6939(9)	0.3069(5)	0.9563(3)	0.079(4)
C14	0.7572(9)	0.2420(5)	0.9985(3)	0.087(4)
C15	0.7683(9)	0.1538(5)	0.9896(3)	0.121(4)
C16	0.7161(9)	0.1305(5)	0.9385(3)	0.117(4)
C17	0.8013	0.2459	1.1009	0.0500 *
C18	0.8635(10)	0.2762(7)	1.1452(4)	0.041(4)
C19	0.9228(10)	0.2266(7)	1.1952(4)	0.200(4)
C110	0.9733(10)	0.2680(7)	1.2394(4)	0.157(4)
C111	0.9645(10)	0.3589(7)	1.2337(4)	0.036(4)
C112	0.9053(10)	0.4084(7)	1.1838(4)	0.159(4)
C113	0.8548(10)	0.3671(7)	1.1395(4)	0.152(4)
C21	0.5070(8)	0.1580(4)	0.7206(2)	0.061(4)
C22	0.6042(8)	0.2178(4)	0.7145(2)	0.077(4)
C23	0.6318(8)	0.2573(4)	0.6600(2)	0.063(4)

Table 10. Positional Parameters (Å) for 2f. (cont).

Atom	X	Y	Z	U(1,1)
C24	0.5622(8)	0.2372(4)	0.6116(2)	0.049(4)
C25	0.4650(8)	0.1774(4)	0.6177(2)	0.069(4)
C26	0.4374(8)	0.1379(4)	0.6722(2)	0.072(4)
C27	0.6697	0.3593	0.5478	0.0500 *
C28	0.6966(8)	0.3593(5)	0.4862(3)	0.049(4)
C29	0.8307(8)	0.3343(5)	0.4602(3)	0.050(4)
C210	0.8489(8)	0.3582(5)	0.4017(3)	0.071(4)
C211	0.7329(8)	0.4070(5)	0.3691(3)	0.070(4)
C212	0.5988(8)	0.4319(5)	0.3950(3)	0.058(4)
C213	0.5807(8)	0.4081(5)	0.4536(3)	0.062(4)
C31	0.2772(10)	0.1040(6)	1.0116(3)	0.060(4)
C32	0.4190(10)	0.1191(6)	1.0201(3)	0.140(4)
C33	0.4575(10)	0.1469(6)	1.0719(3)	0.152(4)
C34	0.3543(10)	0.1597(6)	1.1153(3)	0.080(4)
C35	0.2125(10)	0.1447(6)	1.1069(3)	0.084(4)
C36	0.1740(10)	0.1168(6)	1.0550(3)	0.073(4)
C37	-0.3666	-0.1406	0.7816	0.0500 *
C38	-0.4354(9)	-0.1578(6)	0.7346(3)	0.118(4)
C39	-0.4033(9)	-0.1111(6)	0.6831(3)	0.087(4)
C310	-0.4764(9)	-0.1190(6)	0.6325(3)	0.096(4)
C311	-0.5815(9)	-0.1737(6)	0.6333(3)	0.103(4)
C312	-0.6136(9)	-0.2203(6)	0.6848(3)	0.095(4)
C313	-0.5406(9)	-0.2124(6)	0.7355(3)	0.102(4)
C41	0.1105(9)	0.0162(5)	0.8284(3)	0.097(4)
C42	0.2016(9)	-0.0135(5)	0.7843(3)	0.071(4)
C43	0.1431(9)	-0.0193(5)	0.7303(3)	0.082(4)
C44	-0.0066(9)	0.0046(5)	0.7204(3)	0.077(4)
C45	-0.0977(9)	0.0343(5)	0.7646(3)	0.065(4)
C46	-0.0392(9)	0.0401(5)	0.8186(3)	0.083(4)
C47	0.0371	-0.0237	0.6181	0.0500 *
C48	-0.0970(9)	-0.0316(6)	0.5748(3)	0.065(4)
C49	-0.1988(9)	0.0432(6)	0.5587(3)	0.077(4)
C410	-0.2927(9)	0.0446(6)	0.5122(3)	0.081(4)
C411	-0.2847(9)	-0.0287(6)	0.4819(3)	0.077(4)

Table 10. Positional Parameters (Å) for 2f (cont).

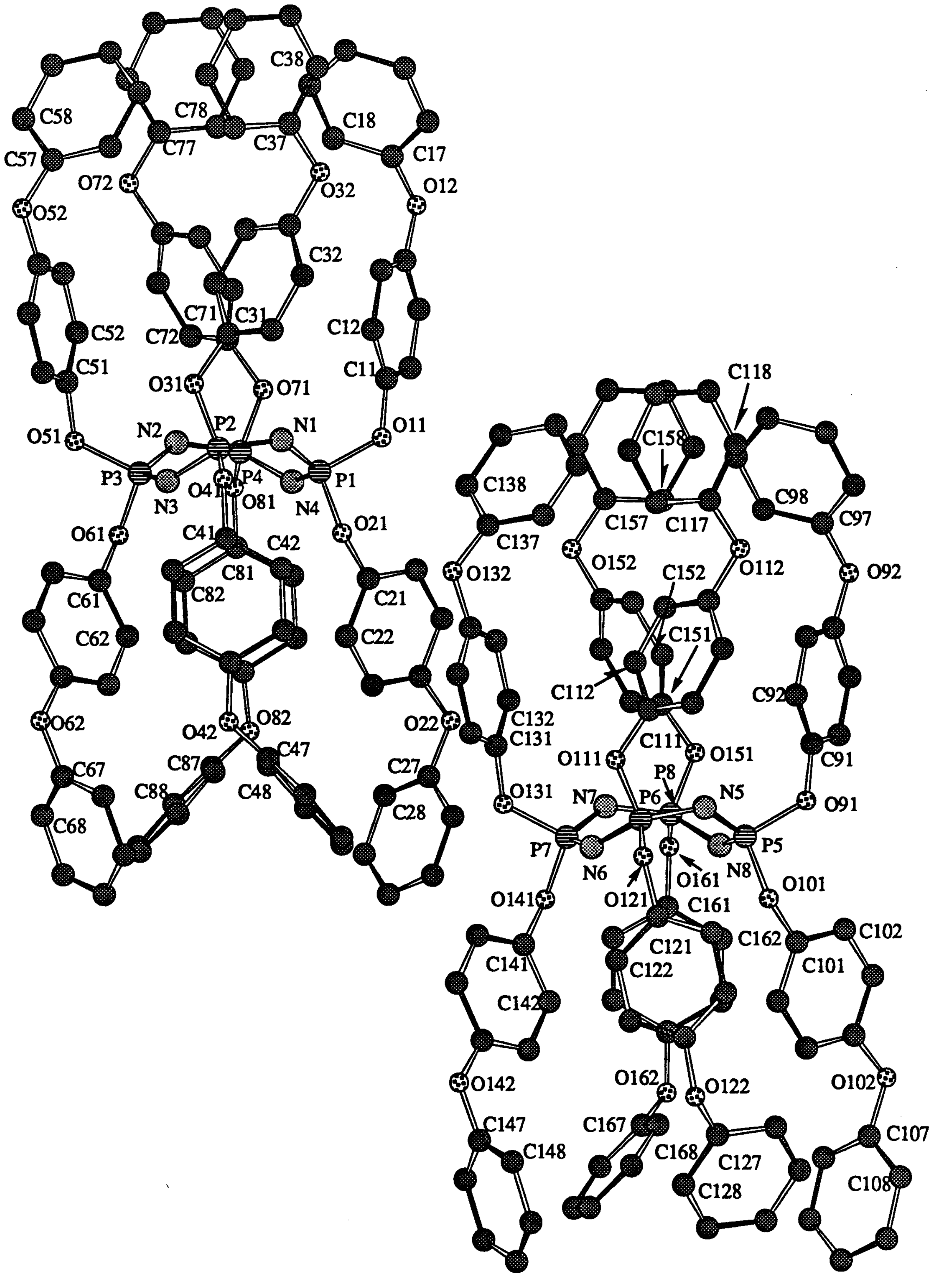
Atom	X	Y	Z	U(1,1)
C412	-0.1828(9)	-0.1035(6)	0.4980(3)	0.105(4)
C413	-0.0890(9)	-0.1049(6)	0.5445(3)	0.081(4)
C51	0.1778(10)	0.3715(5)	0.9123(3)	0.105(4)
C52	0.3006(10)	0.4122(5)	0.9133(3)	0.072(4)
C53	0.3444(10)	0.4392(5)	0.9646(3)	0.086(4)
C54	0.2655(10)	0.4254(5)	1.0149(3)	0.151(4)
C55	0.1428(10)	0.3847(5)	1.0139(3)	0.213(4)
C56	0.0989(10)	0.3577(5)	0.9626(3)	0.161(4)
C57	0.2305	0.4412	1.1132	0.0500 *
C58	0.3112(11)	0.4786(6)	1.1610(3)	0.171(4)
C59	0.2299(11)	0.5476(6)	1.1869(3)	0.108(4)
C510	0.2927(11)	0.5858(6)	1.2299(3)	0.093(4)
C511	0.4370(11)	0.5550(6)	1.2469(3)	0.145(4)
C512	0.5184(11)	0.4861(6)	1.2209(3)	0.148(4)
C513	0.4555(11)	0.4479(6)	1.1780(3)	0.205(5)
C61	0.0965(8)	0.2831(5)	0.7295(2)	0.045(4)
C62	0.1746(8)	0.3481(5)	0.7073(2)	0.059(4)
C63	0.1902(8)	0.3648(5)	0.6479(2)	0.066(4)
C64	0.1277(8)	0.3165(5)	0.6107(2)	0.031(4)
C65	0.0496(8)	0.2514(5)	0.6329(2)	0.044(4)
C66	0.0340(8)	0.2347(5)	0.6923(2)	0.044(4)
C67	0.2027	0.3910	0.5241	0.0500 *
C68	0.2043(8)	0.3999(5)	0.4640(3)	0.041(4)
C69	0.1554(8)	0.4807(5)	0.4328(3)	0.041(4)
C610	0.1590(8)	0.4885(5)	0.3727(3)	0.047(4)
C611	0.2115(8)	0.4155(5)	0.3439(3)	0.038(4)
C612	0.2605(8)	0.3348(5)	0.3751(3)	0.057(4)
C613	0.2568(8)	0.3270(5)	0.4352(3)	0.050(4)

The form of the anisotropic thermal parameter is:

$U = \exp[-2\Pi^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3)$

$+ 2klbcU(2,3))\}]$ where a, b and c are reciprocal lattice constants

* Starred Atoms were refined only isotropically.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C11
C118
O31
O71
O51
N2
P2
N1
O11
C158
P3
P4
P1
C138
C98
O41
O81
N3
N4
C157
C117
C97
O61
C41
O21
C137
C42
O152
O112
O92
O132
C152
C81
C82
C61
C21
C151
C62
C22
C112
C92
C132
O42
O82
O22
C131
O62
C47
C111
O111
O151
C87
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C67
P8
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C88
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C122
C142
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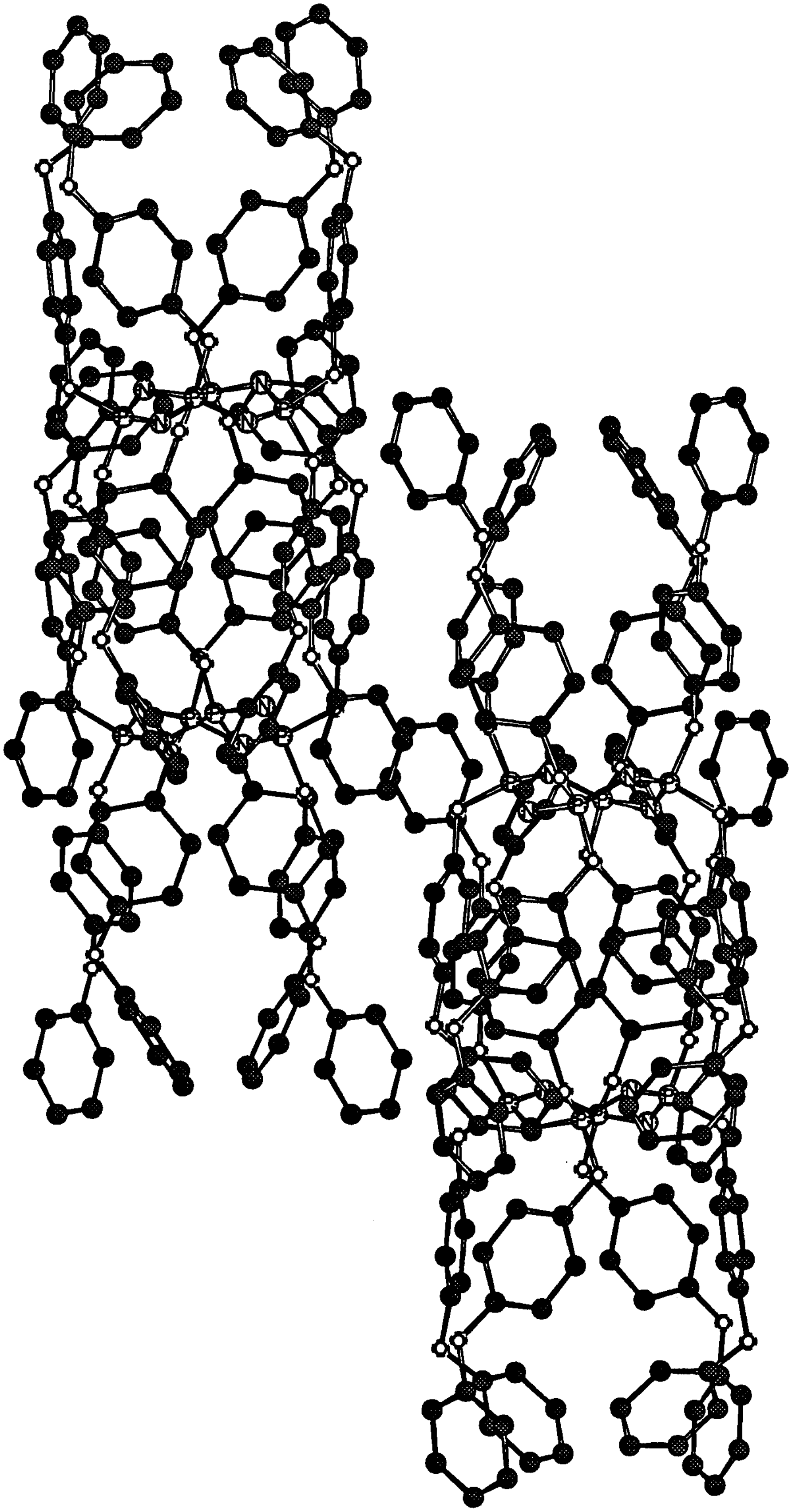
O122
O142
O102
C167
C147
C107
C168
C127
C148
C128
C108

4a

Figure 7



4a Packing Arrangement

Figure 8

Table 11. Bond Distances (Å) and Bond Angles (deg) for 4a (2 Conformations).

P1-N1	1.566(12)	O21-C21	1.389(11)
P1-N4	1.560(9)	O22-C24	1.358(14)
P1-O11	1.581(10)	O22-C27	1.363(14)
P1-O21	1.584(9)	O31-C31	1.357(11)
P2-N1	1.557(13)	O32-C34	1.367(12)
P2-N2	1.531(9)	O32-C37	1.364(16)
P2-O31	1.566(11)	O41-C41	1.377(13)
P2-O41	1.584(9)	O42-C44	1.380(15)
P3-N2	1.584(9)	O42-C47	1.348(15)
P3-N3	1.553(12)	O51-C51	1.371(11)
P3-O51	1.597(10)	O52-C54	1.372(13)
P3-O61	1.574(8)	O52-C57	1.347(14)
P4-N3	1.567(13)	O61-C61	1.383(11)
P4-N4	1.553(10)	O62-C64	1.361(13)
P4-O71	1.547(10)	O62-C67	1.356(14)
P4-O81	1.564(9)	O71-C71	1.367(11)
P5-N5	1.575(12)	O72-C74	1.372(13)
P5-N8	1.560(9)	O72-C77	1.347(15)
P5-O91	1.581(10)	O81-C81	1.357(12)
P5-O101	1.573(9)	O82-C84	1.363(19)
P6-N5	1.543(12)	O82-C87	1.267(18)
P6-N6	1.544(10)	O91-C91	1.377(10)
P6-O111	1.573(10)	O92-C94	1.359(13)
P6-O121	1.581(9)	O92-C97	1.355(15)
P7-N6	1.587(9)	O101-C101	1.383(13)
P7-N7	1.556(12)	O102-C104	1.362(14)
P7-O131	1.599(10)	O102-C107	1.364(14)
P7-O141	1.560(8)	O111-C111	1.351(13)
P8-N7	1.562(13)	O112-C114	1.371(14)
P8-N8	1.565(10)	O112-C117	1.344(14)
P8-O151	1.556(10)	O121-C121	1.371(12)
P8-O161	1.573(9)	O122-C124	1.364(14)
O11-C11	1.371(11)	O122-C127	1.349(14)
O12-C14	1.366(13)	O131-C131	1.386(13)
O12-C17	1.354(16)	O132-C134	1.371(14)

Table 11. Bond Distances (Å) and Bond Angles (deg) for 4a (cont).

O132-C137	1.339(14)	O152-C154	1.363(13)
O141-C141	1.380(10)	O152-C157	1.321(14)
O142-C144	1.376(13)	O161-C161	1.362(13)
O142-C147	1.354(15)	O162-C164	1.367(14)
O151-C151	1.378(14)	O162-C167	1.347(14)

N1-P1-N4	120.0(6)	N5-P6-N6	121.2(6)
N1-P1-O11	107.1(6)	N5-P6-O111	107.9(6)
N4-P1-O11	111.1(6)	N6-P6-O111	107.8(6)
N1-P1-O21	107.4(5)	N5-P6-O121	111.2(5)
N4-P1-O21	109.6(5)	N6-P6-O121	106.8(5)
O11-P1-O21	99.6(5)	O111-P6-O121	99.7(5)
N1-P2-N2	120.9(6)	N6-P7-N7	121.1(6)
N1-P2-O31	108.3(6)	N6-P7-O131	110.5(6)
N2-P2-O31	107.9(6)	N7-P7-O131	107.4(5)
N1-P2-O41	111.7(6)	N6-P7-O141	108.2(6)
N2-P2-O41	107.1(5)	N7-P7-O141	108.8(5)
O31-P2-O41	98.4(5)	O131-P7-O141	98.6(5)
N2-P3-N3	120.8(6)	N7-P8-N8	120.4(6)
N2-P3-O51	110.7(5)	N7-P8-O151	108.7(6)
N3-P3-O51	107.7(5)	N8-P8-O151	107.9(5)
N2-P3-O61	108.0(5)	N7-P8-O161	110.1(5)
N3-P3-O61	108.8(5)	N8-P8-O161	107.2(5)
O51-P3-O61	98.6(5)	O151-P8-O161	100.7(5)
N3-P4-N4	120.1(6)	P1-N1-P2	135.4(7)
N3-P4-O71	108.7(6)	P2-N2-P3	136.2(7)
N4-P4-O71	107.9(6)	P3-N3-P4	135.9(7)
N3-P4-O81	110.4(5)	P1-N4-P4	135.2(8)
N4-P4-O81	107.4(6)	P5-N5-P6	136.4(6)
O71-P4-O81	100.7(5)	P6-N6-P7	132.8(7)
N5-P5-N8	120.3(6)	P7-N7-P8	135.4(7)
N5-P5-O91	107.5(5)	P5-N8-P8	134.4(8)
N8-P5-O91	110.6(5)	P1-O11-C11	124.2(7)
N5-P5-O101	108.6(5)	C14-O12-C17	119.7(11)
N8-P5-O101	108.2(5)	P1-O21-C21	124.3(6)
O91-P5-O101	99.6(5)	C24-O22-C27	119.3(10)

Table 11. Bond Distances (Å) and Bond Angles (deg) for 4a (cont).

P2-O31-C31	123.9(9)
C34-O32-C37	117.8(11)
P2-O41-C41	124.5(7)
C44-O42-C47	118.4(9)
P3-O51-C51	123.9(7)
C54-O52-C57	118.4(11)
P3-O61-C61	123.3(6)
C64-O62-C67	120.2(10)
P4-O71-C71	126.5(8)
C74-O72-C77	117.0(10)
P4-O81-C81	121.5(6)
C84-O82-C87	117.1(12)
P5-O91-C91	122.9(7)
C94-O92-C97	117.6(10)
P5-O101-C101	124.29(10)
C104-O102-C107	117.9(10)
P6-O111-C111	123.9(10)
C114-O112-C117	117.8(9)
P6-O121-C121	120.9(6)
C124-O122-C127	118.3(10)
P7-O131-C131	123.8(9)
C134-O132-C137	118.3(9)
P7-O141-C141	124.2(5)
C144-O142-C147	119.6(10)
P8-O151-C151	121.4(10)
C154-O152-C157	116.3(5)
P8-O161-C161	126.4(9)
C164-O162-C167	118.3(6)
O11-C11-C12	121.2(7)
O11-C11-C16	118.6(7)
O12-C14-C13	124.2(8)
O12-C14-C15	120.0(6)
O12-C17-C18	119.5(8)
O12-C17-C12	120.5(9)
O21-C21-C22	122.7(7)
O21-C21-C26	117.2(7)
O22-C24-C23	114.9(8)
O22-C24-C25	125.0(8)
O22-C27-C28	118.9(8)
O22-C27-C212	120.9(8)
O31-C31-C32	116.9(6)
O31-C31-C36	123.0(7)
O32-C34-C33	122.2(7)
O32-C34-C35	117.7(7)
O32-C37-C38	115.8(9)
O32-C37-C312	124.2(9)
O41-C41-C42	120.9(8)
O41-C41-C46	118.8(7)
O42-C44-C43	120.2(8)
O42-C44-C45	119.4(8)
O42-C47-C48	118.9(10)
O42-C47-C412	120.9(10)
O51-C51-C52	121.6(7)
O51-C51-C56	118.2(7)
O52-C54-C53	123.1(7)
O52-C54-C55	116.7(8)
O52-C57-C58	117.6(8)
O52-C57-C512	122.4(8)
O61-C61-C62	117.8(7)
O61-C61-C66	122.2(7)
O62-C64-C63	125.7(8)
O62-C64-C65	122.2(7)
O62-C67-C68	118.0(7)
O62-C67-C612	121.9(7)
O71-C71-C72	117.9(6)
O71-C71-C76	122.0(7)
O72-C74-C73	121.9(7)
O72-C74-C75	118.1(6)
O72-C77-C78	121.9(10)
O72-C77-C712	117.9(10)

Table 11. Bond Distances (Å) and Bond Angles (deg) for 4a (cont).

O81-C81-C82	118.2(8)	O122-C124-C125	119.4(10)
O81-C81-C86	121.8(8)	O122-C127-C128	118.9(8)
O82-C84-C83	121.2(10)	O122-C127-C1212	120.9(8)
O82-C84-C85	118.6(10)	O131-C131-C132	121.5(9)
O82-C87-C88	124.0(11)	O131-C131-C136	118.2(7)
O82-C87-C812	115.8(10)	O132-C134-C133	123.1(9)
O91-C91-C92	121.7(7)	O132-C134-C135	116.7(9)
O91-C91-C96	118.2(7)	O132-C137-C138	119.0(9)
O92-C94-C93	125.1(7)	O132-C137-C1312	120.9(8)
O92-C94-C95	114.8(8)	O141-C141-C142	117.6(7)
O92-C97-C98	120.8(8)	O141-C141-C146	122.3(7)
O92-C97-C912	119.1(9)	O142-C144-C143	124.7(8)
O101-C101-C102	122.7(8)	O142-C144-C145	115.3(8)
O101-C101-C106	117.9(9)	O142-C147-C148	122.2(8)
O102-C104-C103	125.0(8)	O142-C147-C1412	117.6(7)
O102-C104-C105	114.9(8)	O151-C151-C152	117.8(8)
O102-C107-C108	120.0(8)	O151-C151-C156	122.0(9)
O102-C107-C1012	119.9(8)	O152-C154-C153	117.8(6)
O111-C111-C112	116.9(7)	O152-C154-C155	122.2(7)
O111-C111-C116	122.9(8)	O152-C157-C158	124.6(10)
O112-C114-C113	122.1(7)	O152-C157-C1512	115.3(10)
O112-C114-C115	117.7(8)	O161-C161-C162	118.2(8)
O112-C117-C118	115.8(7)	O161-C161-C166	121.6(10)
O112-C117-C1112	124.2(8)	O162-C164-C163	121.1(8)
O121-C121-C122	120.8(8)	O162-C164-C165	118.7(9)
O121-C121-C126	119.1(8)	O162-C167-C168	124.0(7)
O122-C124-C123	120.2(9)	O162-C167-C1612	115.7(9)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Phenoxy ring carbons are set to a C-C bond distance of 1.395 Å and a C-C-C bond angle of 120.0°in the x-ray crystal refinement program.

Table 12. Positional Parameters (Å) for 4a
(2 conformations)

Atom	X	Y	Z	U(1,1)
P1	0.1463(2)	0.2461(2)	0.7652(1)	0.050(2)
P2	0.1256(2)	0.3613(2)	0.7257(1)	0.045(2)
P3	0.0000(2)	0.2651(2)	0.6428(1)	0.046(2)
P4	0.0635(2)	0.1520(2)	0.6629(1)	0.058(2)
P5	0.1535(2)	0.2280(2)	0.2636(1)	0.044(2)
P6	0.1440(2)	0.3461(2)	0.2246(1)	0.041(2)
P7	0.0109(2)	0.2576(2)	0.1452(1)	0.047(2)
P8	0.0661(2)	0.1388(2)	0.1607(1)	0.055(2)
N1	0.1721(6)	0.3139(5)	0.7478(4)	0.085(4)
N2	0.0409(6)	0.3316(5)	0.6921(4)	0.069(3)
N3	0.0366(6)	0.1994(5)	0.6298(4)	0.099(3)
N4	0.0861(6)	0.1809(5)	0.7256(4)	0.093(3)
N5	0.1842(6)	0.2959(5)	0.2466(4)	0.071(3)
N6	0.0557(6)	0.3228(5)	0.1946(4)	0.070(3)
N7	0.0443(6)	0.1900(5)	0.1299(4)	0.103(4)
N8	0.0910(6)	0.1645(5)	0.2238(4)	0.090(3)
O11	0.2281(5)	0.2271(5)	0.7844(3)	0.028(3)
O12	0.4550(5)	0.1211(6)	0.6591(5)	0.061(3)
O21	0.1113(5)	0.2671(4)	0.8218(3)	0.043(3)
O22	-0.0533(6)	0.0878(6)	0.9254(5)	0.062(3)
O31	0.1833(5)	0.3983(5)	0.6918(4)	0.017(3)
O32	0.5090(6)	0.3937(6)	0.6746(5)	0.039(3)
O41	0.1188(6)	0.4281(4)	0.7724(4)	0.058(4)
O42	-0.0736(8)	0.4561(5)	0.9408(5)	0.124(4)
O51	-0.0108(5)	0.2860(4)	0.5878(3)	0.026(3)
O52	0.2282(6)	0.3732(6)	0.4679(4)	0.074(3)
O61	-0.0935(5)	0.2433(4)	0.6497(3)	0.021(3)
O62	-0.2753(6)	0.4291(5)	0.7503(4)	0.084(3)
O71	0.1368(5)	0.1242(5)	0.6386(3)	0.052(3)
O72	0.2264(7)	0.0864(7)	0.4313(4)	0.079(4)
O81	-0.0028(5)	0.0825(4)	0.6508(4)	0.046(3)
O82	-0.2745(9)	0.0532(6)	0.7597(7)	0.147(4)

Table 12. Positional Parameters (Å) for 4a (cont).

Atom	X	Y	Z	U(1,1)
O91	0.2320(5)	0.2047(4)	0.2830(3)	0.019(3)
O92	0.4549(6)	0.1004(5)	0.1529(5)	0.063(3)
O101	0.1173(5)	0.2487(4)	0.3192(3)	0.036(3)
O102	0.0600(6)	0.9193(5)	0.5735(5)	0.060(3)
O111	0.2022(5)	0.3743(5)	0.1862(4)	0.012(3)
O112	0.5313(6)	0.3800(6)	0.1757(5)	0.032(3)
O121	0.1481(5)	0.4164(4)	0.2707(4)	0.044(3)
O122	0.0870(8)	0.5485(5)	0.5892(5)	0.157(4)
O131	-0.0011(5)	0.2800(4)	0.0910(3)	0.034(3)
O132	0.2408(7)	0.3851(5)	-0.0203(5)	0.078(3)
O141	-0.0813(4)	0.2383(4)	0.1538(3)	0.014(3)
O142	-0.2594(7)	0.4227(5)	0.2632(4)	0.091(3)
O151	0.1356(5)	0.1061(5)	0.1341(3)	0.048(3)
O152	-0.2273(6)	0.9073(6)	1.0704(4)	0.061(3)
O161	-0.0060(5)	0.0725(4)	0.1479(3)	0.039(3)
O162	-0.2630(7)	0.0401(6)	0.2693(5)	0.081(3)
C11	0.2818(4)	0.2022(4)	0.7500(3)	0.057(4)
C12	0.3388(4)	0.2468(4)	0.7311(3)	0.041(3)
C13	0.3968(4)	0.2209(4)	0.6995(3)	0.059(4)
C14	0.3977(4)	0.1504(4)	0.6868(3)	0.048(4)
C15	0.3406(4)	0.1058(4)	0.7058(3)	0.068(4)
C16	0.2827(4)	0.1317(4)	0.7374(3)	0.052(4)
C17	0.4986(5)	0.1538(4)	0.6274(3)	0.083(3) *
C18	0.4617(5)	0.1510(4)	0.5765(3)	0.107(3) *
C19	0.5070(5)	0.1821(4)	0.5426(3)	0.119(3) *
C110	0.5892(5)	0.2160(4)	0.5595(3)	0.102(3) *
C111	0.6261(5)	0.2187(4)	0.6104(3)	0.101(3) *
C112	0.5808(5)	0.1875(4)	0.6443(3)	0.086(3) *
C21	0.0689(4)	0.2197(3)	0.8455(2)	0.060(4)
C22	0.0975(4)	0.1623(3)	0.8512(2)	0.074(4)
C23	0.0541(4)	0.1186(3)	0.8777(2)	0.079(4)
C24	-0.0179(4)	0.1323(3)	0.8986(2)	0.052(4)
C25	-0.0464(4)	0.1897(3)	0.8929(2)	0.084(4)
C26	-0.0030(4)	0.2334(3)	0.8663(2)	0.059(4)
C27	-0.1262(5)	0.0946(4)	0.9447(3)	0.069(3) *

Table 12. Positional Parameters (Å) for 4a (cont).

Atom	X	Y	Z	U(1,1)
C28	-0.1261(5)	0.1271(4)	1.0000(3)	0.085(3) *
C29	-0.2003(5)	0.1306(4)	1.0214(3)	0.092(3) *
C210	-0.2745(5)	0.1016(4)	0.9875(3)	0.095(3) *
C211	-0.2746(5)	0.0691(4)	0.9323(3)	0.112(3) *
C212	-0.2005(5)	0.0656(4)	0.9109(3)	0.099(3) *
C31	0.2636(4)	0.3961(4)	0.6899(3)	0.087(4)
C32	0.2845(4)	0.3580(4)	0.6408(3)	0.056(4)
C33	0.3667(4)	0.3571(4)	0.6348(3)	0.085(4)
C34	0.4279(4)	0.3943(4)	0.6779(3)	0.063(4)
C35	0.4070(4)	0.4324(4)	0.7270(3)	0.061(4)
C36	0.3248(4)	0.4333(4)	0.7329(3)	0.066(4)
C37	0.5479(5)	0.4256(4)	0.6402(3)	0.068(3) *
C38	0.6185(5)	0.4041(4)	0.6231(3)	0.092(3) *
C39	0.6642(5)	0.4355(4)	0.5894(3)	0.118(3) *
C310	0.6392(5)	0.4884(4)	0.5729(3)	0.117(3) *
C311	0.5686(5)	0.5099(4)	0.5900(3)	0.115(3) *
C312	0.5230(5)	0.4785(4)	0.6236(3)	0.082(3) *
C41	0.0688(5)	0.4274(4)	0.8128(3)	0.084(4)
C42	-0.0157(5)	0.4207(4)	0.8021(3)	0.076(4)
C43	-0.0640(5)	0.4279(4)	0.8447(3)	0.102(4)
C44	-0.0279(5)	0.4417(4)	0.8980(3)	0.101(4)
C45	0.0566(5)	0.4484(4)	0.9087(3)	0.110(4)
C46	0.1049(5)	0.4413(4)	0.8661(3)	0.091(4)
C47	-0.1178(6)	0.4023(5)	0.9546(3)	0.079(3) *
C48	-0.2031(6)	0.3932(5)	0.9511(3)	0.147(4) *
C49	-0.2496(6)	0.3413(5)	0.9691(3)	0.185(4) *
C410	-0.2108(6)	0.2986(5)	0.9908(3)	0.119(3) *
C411	-0.1256(6)	0.3078(5)	0.9943(3)	0.113(3) *
C412	-0.0791(6)	0.3596(5)	0.9763(3)	0.109(3) *
C51	0.0533(4)	0.3060(4)	0.5608(2)	0.051(4)
C52	0.0907(4)	0.2575(4)	0.5279(2)	0.065(4)
C53	0.1510(4)	0.2790(4)	0.4973(2)	0.081(4)
C54	0.1738(4)	0.3491(4)	0.4997(2)	0.082(4)
C55	0.1363(4)	0.3975(4)	0.5326(2)	0.072(4)

Table 12 Positional Parameters (Å) for 4a (cont).

Atom	X	Y	Z	U(1,1)
C56	0.0761(4)	0.3960(4)	0.5632(2)	0.063(4)
C57	0.2956(4)	0.3465(4)	0.4602(3)	0.065(3) *
C58	0.3002(4)	0.3045(4)	0.4082(3)	0.087(3) *
C59	0.3698(4)	0.2775(4)	0.3975(3)	0.105(3) *
C510	0.4347(4)	0.2927(4)	0.4387(3)	0.090(3) *
C511	0.4301(4)	0.3348(4)	0.4907(3)	0.095(3) *
C512	0.3605(4)	0.3618(4)	0.5014(3)	0.088(3) *
C61	-0.1384(4)	0.2902(3)	0.6750(3)	0.084(4)
C62	-0.1823(4)	0.2756(3)	0.7162(3)	0.069(4)
C63	-0.2298(4)	0.3206(3)	0.7423(3)	0.067(4)
C64	-0.2334(4)	0.3802(3)	0.7271(3)	0.058(4)
C65	-0.1895(4)	0.3949(3)	0.6858(3)	0.048(4)
C66	-0.1420(4)	0.3499(3)	0.6598(3)	0.056(4)
C67	-0.3212(5)	0.4207(4)	0.7905(3)	0.071(3) *
C68	-0.2948(5)	0.4658(4)	0.8429(3)	0.078(3) *
C69	-0.3428(5)	0.4619(4)	0.8848(3)	0.095(3) *
C610	-0.4172(5)	0.4131(4)	0.8744(3)	0.094(3) *
C611	-0.4436(5)	0.3680(4)	0.8220(3)	0.094(3) *
C612	-0.3956(5)	0.3718(4)	0.7801(3)	0.082(3) *
C71	0.1552(4)	0.1163(4)	0.5866(3)	0.049(4)
C72	0.2266(4)	0.1591(4)	0.5790(3)	0.083(4)
C73	0.2513(4)	0.1495(4)	0.5272(3)	0.069(4)
C74	0.2046(4)	0.0972(4)	0.4829(3)	0.083(4)
C75	0.1332(4)	0.0545(4)	0.4905(3)	0.080(4)
C76	0.1085(4)	0.0640(4)	0.5423(3)	0.077(4)
C77	0.2992(5)	0.0690(4)	0.4233(4)	0.082(3) *
C78	0.3284(5)	0.0255(4)	0.4494(4)	0.095(3) *
C79	0.4010(5)	0.0044(4)	0.4368(4)	0.129(3) *
C710	0.4445(5)	0.0268(4)	0.3980(4)	0.149(4) *
C711	0.4153(5)	0.0703(4)	0.3719(4)	0.152(4) *
C712	0.3427(5)	0.0913(4)	0.3846(4)	0.128(3) *
C81	-0.0697(4)	0.0783(4)	0.6780(3)	0.077(4)
C82	-0.0625(4)	0.0640(4)	0.7277(3)	0.096(4)
C83	-0.1305(4)	0.0571(4)	0.7561(3)	0.108(4)

Table 12. Positional Parameters (Å) for 4a (cont).

Atom	X	Y	Z	U(1,1)
C84	-0.2057(4)	0.0640(4)	0.7348(3)	0.116(4)
C85	-0.2129(4)	0.0789(4)	0.6851(3)	0.081(4)
C86	-0.1449(4)	0.0858(4)	0.6566(3)	0.067(4)
C87	-0.3065(7)	0.1047(5)	0.7781(4)	0.091(3) *
C88	-0.2639(7)	0.1680(5)	0.8143(4)	0.125(3) *
C89	-0.3057(7)	0.2200(5)	0.8356(4)	0.137(4) *
C810	-0.3901(7)	0.2087(5)	0.8209(4)	0.137(4) *
C811	-0.4327(7)	0.1453(5)	0.7848(4)	0.195(4) *
C812	-0.3908(7)	0.0934(5)	0.7634(4)	0.168(4) *
C91	0.2865(4)	0.1813(4)	0.2483(3)	0.045(4)
C92	0.3455(4)	0.2270(4)	0.2318(3)	0.043(3)
C93	0.4029(4)	0.2017(4)	0.1993(3)	0.050(4)
C94	0.4014(4)	0.1307(4)	0.1835(3)	0.042(4)
C95	0.3424(4)	0.0850(4)	0.2001(3)	0.051(4)
C96	0.2850(4)	0.1103(4)	0.2325(3)	0.057(4)
C97	0.5016(5)	0.1384(4)	0.1257(4)	0.084(3) *
C98	0.4709(5)	0.1421(4)	0.0753(4)	0.102(3) *
C99	0.5212(5)	0.1789(4)	0.0468(4)	0.128(3) *
C910	0.6021(5)	0.2120(4)	0.0688(4)	0.112(3) *
C911	0.6328(5)	0.2083(4)	0.1193(4)	0.113(3) *
C912	0.5826(5)	0.1715(4)	0.1477(4)	0.093(3) *
C101	-0.0720(4)	0.7963(3)	0.6566(3)	0.053(4)
C102	-0.0008(4)	0.7788(3)	0.6369(3)	0.057(4)
C103	0.0460(4)	0.8196(3)	0.6096(3)	0.084(4)
C104	0.0216(4)	0.8779(3)	0.6019(3)	0.077(4)
C105	-0.0496(4)	0.8954(3)	0.6216(3)	0.062(4)
C106	-0.0964(4)	0.8546(3)	0.6490(3)	0.072(4)
C107	0.1337(5)	0.9089(4)	0.5572(3)	0.073(3) *
C108	0.2060(5)	0.9410(4)	0.5926(3)	0.098(3) *
C109	0.2818(5)	0.9335(4)	0.5749(3)	0.121(3) *
C1010	0.2852(5)	0.8940(4)	0.5218(3)	0.100(3) *
C1011	0.2129(5)	0.8620(4)	0.4865(3)	0.100(3) *
C1012	0.1372(5)	0.8694(4)	0.5042(3)	0.087(3) *
C111	-0.2831(4)	0.6254(3)	0.8133(3)	0.068(4)

Table 12 Positional Parameters (Å) for 4a (cont).

Atom	X	Y	Z	U(1,1)
C112	-0.3416(4)	0.5876(3)	0.7688(3)	0.057(4)
C113	-0.4247(4)	0.5859(3)	0.7726(3)	0.057(4)
C114	-0.4494(4)	0.6220(3)	0.8211(3)	0.055(4)
C115	-0.3908(4)	0.6597(3)	0.8656(3)	0.069(4)
C116	-0.3077(4)	0.6614(3)	0.8617(3)	0.069(4)
C117	-0.5691(5)	0.5868(4)	0.8573(3)	0.070(3) *
C118	-0.6436(5)	0.6031(4)	0.8711(3)	0.081(3) *
C119	-0.6891(5)	0.5697(4)	0.9037(3)	0.096(3) *
C1110	-0.6601(5)	0.5200(4)	0.9225(3)	0.103(3) *
C1111	-0.5855(5)	0.5038(4)	0.9087(3)	0.094(3) *
C1112	-0.5400(5)	0.5371(4)	0.8761(3)	0.076(3) *
C121	0.0893(4)	0.4219(4)	0.3055(3)	0.041(4)
C122	0.0975(4)	0.4040(4)	0.3536(3)	0.108(4)
C123	0.0383(4)	0.4120(4)	0.3893(3)	0.138(4)
C124	-0.0291(4)	0.4380(4)	0.3768(3)	0.119(4)
C125	-0.0373(4)	0.4559(4)	0.3286(3)	0.086(4)
C126	0.0219(4)	0.4479(4)	0.2929(3)	0.066(4)
C127	-0.1110(5)	0.4087(4)	0.4411(3)	0.081(3) *
C128	-0.1489(5)	0.3387(4)	0.4173(3)	0.106(3) *
C129	-0.1803(5)	0.2979(4)	0.4498(3)	0.108(3) *
C1210	-0.1738(5)	0.3271(4)	0.5061(3)	0.094(3) *
C1211	-0.1359(5)	0.3970(4)	0.5299(3)	0.100(3) *
C1212	-0.1045(5)	0.4378(4)	0.4974(3)	0.089(3) *
C131	-0.0644(4)	0.6956(4)	0.9341(3)	0.066(4)
C132	-0.1037(4)	0.7408(4)	0.9688(3)	0.074(4)
C133	-0.1638(4)	0.7148(4)	0.9976(3)	0.076(4)
C134	-0.1847(4)	0.6436(4)	0.9916(3)	0.082(4)
C135	-0.1454(4)	0.5984(4)	0.9569(3)	0.081(4)
C136	-0.0853(4)	0.6244(4)	0.9281(3)	0.075(4)
C137	0.3034(5)	0.3549(4)	-0.0346(4)	0.079(3) *
C138	0.3042(5)	0.3198(4)	-0.0892(4)	0.089(3) *
C139	0.3714(5)	0.2919(4)	-0.1056(4)	0.104(3) *
C1310	0.4377(5)	0.2991(4)	-0.0673(4)	0.098(3) *
C1311	0.4369(5)	0.3343(4)	-0.0127(4)	0.102(3) *

Table 12. Positional Parameters (Å) for 4a (cont).

Atom	X	Y	Z	U(1,1)
C1312	0.3698(5)	0.3622(4)	0.0037(4)	0.099(3) *
C141	-0.1239(4)	0.2854(3)	0.1815(3)	0.044(4)
C142	-0.1653(4)	0.2697(3)	0.2234(3)	0.063(4)
C143	-0.2117(4)	0.3144(3)	0.2515(3)	0.087(4)
C144	-0.2167(4)	0.3746(3)	0.2375(3)	0.055(4)
C145	-0.1754(4)	0.3902(3)	0.1956(3)	0.051(4)
C146	-0.1290(4)	0.3456(3)	0.1676(3)	0.048(4)
C147	-0.3051(5)	0.4102(4)	0.3024(3)	0.073(3) *
C148	-0.3829(5)	0.3659(4)	0.2903(3)	0.094(3) *
C149	-0.4299(5)	0.3585(4)	0.3321(3)	0.099(3) *
C1410	-0.3990(5)	0.3954(4)	0.3860(3)	0.098(3) *
C1411	-0.3212(5)	0.4398(4)	0.3981(3)	0.115(3) *
C1412	-0.2743(5)	0.4472(4)	0.3564(3)	0.098(3) *
C151	-0.1562(4)	0.8952(4)	0.9171(3)	0.054(4)
C152	-0.1074(4)	0.9413(4)	0.9636(3)	0.057(4)
C153	-0.1325(4)	0.9451(4)	1.0148(3)	0.071(4)
C154	-0.2064(4)	0.9029(4)	1.0195(3)	0.057(4)
C155	-0.2551(4)	0.8568(4)	0.9729(3)	0.061(4)
C156	-0.2300(4)	0.8529(4)	0.9217(3)	0.058(4)
C157	-0.2992(5)	0.9225(4)	1.0800(3)	0.080(3) *
C158	-0.3339(5)	0.9668(4)	1.0578(3)	0.084(3) *
C159	-0.4081(5)	0.9825(4)	1.0730(3)	0.128(3) *
C1510	-0.4475(5)	0.9539(4)	1.1104(3)	0.141(4) *
C1511	-0.4128(5)	0.9096(4)	1.1326(3)	0.155(4) *
C1512	-0.3386(5)	0.8939(4)	1.1174(3)	0.113(3) *
C161	0.0692(4)	0.9316(4)	0.8215(3)	0.068(4)
C162	0.1451(4)	0.9212(4)	0.8389(3)	0.067(4)
C163	0.2106(4)	0.9291(4)	0.8085(3)	0.075(4)
C164	0.2002(4)	0.9473(4)	0.7606(3)	0.091(4)
C165	0.1243(4)	0.9577(4)	0.7432(3)	0.080(4)
C166	0.0588(4)	0.9498(4)	0.7736(3)	0.078(4)
C167	0.3133(5)	0.9152(5)	0.7223(3)	0.082(3) *
C168	0.3967(5)	0.9415(5)	0.7410(3)	0.095(3) *
C169	0.4522(5)	0.8985(5)	0.7288(3)	0.106(3) *

Table 12. Positional Parameters (Å) for 4a (cont).

Atom	X	Y	Z	U(1,1)
C1610	0.4244(5)	0.8292(5)	0.6977(3)	0.106(3) *
C1611	0.3411(5)	0.8028(5)	0.6789(3)	0.108(3) *
C1612	0.2855(5)	0.8458(5)	0.6912(3)	0.096(3) *

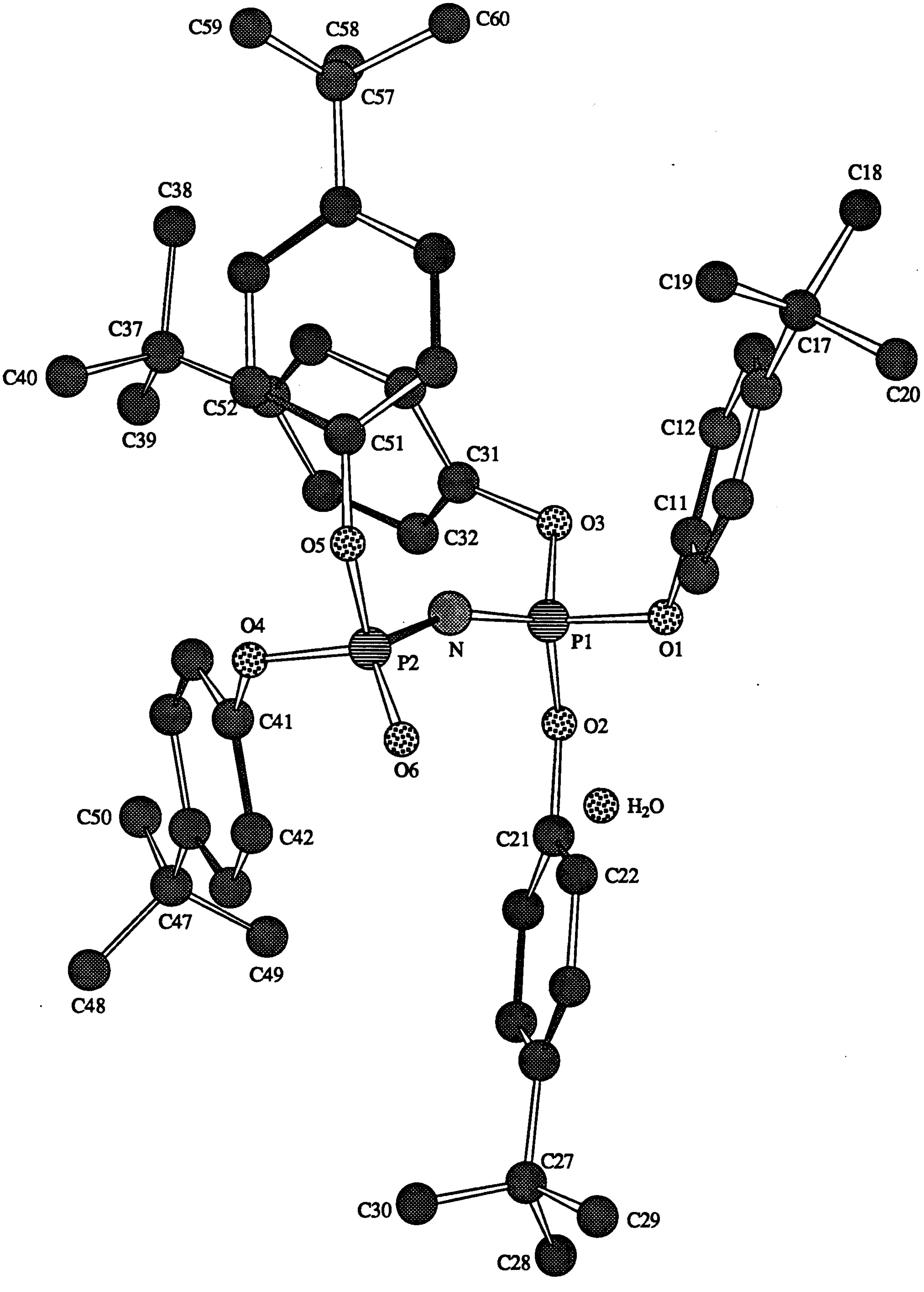
Numbers in parentheses are estimated standard deviations in the least significant digits.

The form of the anisotropic thermal parameter is:

$U = \exp[-2\pi^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3)$

$+ 2klbcU(2,3))\}]$ where a, b, and c are reciprocal lattice constants

* Starred Atoms were refined only isotropically.


C59
C58
C60
C57
C38
C18
C19
C37
C17
C40
C20
C52
C12
C39
C51
C31
C11
O3
O5
C32
O4
N
P1
O1
P2
C41
O2
O6
H$_2$O
C50
C42
C21
C22
C47
C49
C48
C27
C30
C29
C28

6a

Figure 9

Table 13. Bond Distances (Å) and Bond Angles (deg) for 6a.

P1-N	1.495(4)	C24-C27	1.511(8)
P1-O1	1.548(3)	C27-C28	1.496(9)
P1-O2	1.539(3)	C27-C29	1.448(20)
P1-O3	1.562(4)	C27-C30	1.405(15)
P2-N	1.578(5)	C34-C37	1.517(8)
P2-O4	1.578(4)	C37-C38	1.532(14)
P2-O5	1.582(3)	C37-C39	1.525(16)
P2-O6	1.449(5)	C37-C40	1.508(20)
O1-C11	1.408(4)	C44-C47	1.507(9)
O2-C21	1.410(5)	C47-C48	1.416(13)
O3-C31	1.398(5)	C47-C49	1.408(16)
O4-C41	1.388(6)	C47-C50	1.437(23)
O5-C51	1.378(5)	C54-C57	1.536(8)
C14-C17	1.498(7)	C57-C58	1.549(17)
C17-C18	1.501(11)	C57-C59	1.362(16)
C17-C19	1.369(12)	C57-C60	1.546(13)
C17-C20	1.495(15)		

N-P1-O1	118.8(2)	P2-O4-C41	121.5(3)
N-P1-O2	118.4(2)	P2-O5-C51	124.5(4)
O1-P1-O2	101.4(2)	O1-C11-C12	121.0(4)
N-P1-O3	113.3(2)	O1-C11-C16	118.8(3)
O1-P1-O3	102.1(2)	C13-C14-C17	120.3(4)
O2-P1-O3	101.1(3)	C15-C14-C17	119.7(5)
N-P2-O4	106.3(2)	C14-C17-C18	114.7(7)
N-P2-O5	109.2(2)	C14-C17-C19	112.6(6)
O4-P2-O5	99.2(2)	C18-C17-C19	111.1(7)
N-P2-O6	119.4(2)	C14-C17-C20	110.6(6)
O4-P2-O6	114.4(2)	C18-C17-C20	96.7(9)
O5-P2-O6	106.5(3)	C19-C17-C20	110.0(10)
P1-N-P2	157.0(3)	O2-C21-C22	124.1(3)
P1-01-C11	121.3(2)	O2-C21-C26	115.9(4)
P1-O2-C21	127.0(3)	C23-C24-C27	120.6(4)
P1-O3-C31	121.2(3)	C25-C24-C27	119.4(4)

Table 13. Bond Distances (Å) and Bond Angles (deg) for 6a (cont).

C24-C27-C28	112.6(6)	C43-C44-C47	120.6(5)
C24-C27-C29	111.1(7)	C45-C44-C47	119.3(5)
C28-C27-C29	106.2(8)	C44-C47-C48	111.9(9)
C24-C27-C30	109.4(8)	C44-C47-C49	115.7(8)
C28-C27-C30	110.9(8)	C48-C47-C49	105.5(10)
C29-C27-C30	106.4(12)	C44-C47-C50	117.1(7)
O3-C31-C32	120.5(3)	C48-C47-C50	106.8(13)
O3-C31-C36	119.5(3)	C49-C47-C50	98.5(11)
C33-C34-C37	120.6(4)	O5-C51-C52	122.6(3)
C35-C34-C37	120.6(4)	O5-C51-C56	117.1(4)
C34-C37-C38	109.1(6)	C53-C54-C57	120.0(4)
C34-C37-C39	113.1(6)	C55-C54-C57	120.0(4)
C38-C37-C39	106.2(10)	C54-C57-C58	106.6(6)
C34-C37-C40	107.9(8)	C54-C57-C59	114.2(9)
C38-C37-C40	110.8(8)	C58-C57-C59	116.1(11)
C39-C37-C40	109.7(10)	C54-C57-C60	112.9(7)
O4-C41-C42	122.7(5)	C58-C57-C60	93.6(9)
O4-C41-C46	117.3(3)	C59-C57-C60	111.7(8)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Phenoxy ring carbons are set to a C-C bond distance of 1.395 Å and a C-C-C bond angle of 120.0°in the x-ray crystal refinement program.

Table 14. Positional Parameters (Å) for 6a.

Atom	X	Y	Z	U (1,1) (x 10^3)
P1	0.3411(1)	0.3953(1)	0.7613(1)	63(1)
P2	0.2590(1)	0.5285(1)	0.8837(1)	67(1)
N	0.2792(3)	0.4660(3)	0.8121(3)	72(3)
O1	0.4389(2)	0.4231(2)	0.7011(2)	64(2)
O2	0.3880(3)	0.2838(3)	0.8209(2)	92(2)
O3	0.2742(3)	0.3830(3)	0.6864(2)	75(2)
O4	0.1638(3)	0.4972(3)	0.9508(3)	102(3)
O5	0.2029(3)	0.6431(3)	0.8285(3)	98(3)
O6	0.3479(3)	0.5299(3)	0.9340(3)	92(3)
O7(W)	0.5583(3)	0.5501(4)	0.8817(3)	101(3)
C11	0.4341(3)	0.5224(3)	0.6386(2)	57(3)
C12	0.3900(3)	0.5565(3)	0.5475(2)	88(4)
C13	0.3940(3)	0.6522(3)	0.4840(2)	92(4)
C14	0.4420(3)	0.7137(3)	0.5115(2)	73(3)
C15	0.4860(3)	0.6796(3)	0.6025(2)	91(4)
C16	0.4821(3)	0.5839(3)	0.6661(2)	83(4)
C17	0.4478(5)	0.8159(5)	0.4431(5)	102(5)
C18	0.4287(10)	0.8318(7)	0.3401(5)	379(17)
C19	0.3853(12)	0.8940(6)	0.4710(7)	483(23)
C20	0.5603(10)	0.8246(9)	0.4302(10)	209(13)
C21	0.4518(3)	0.2478(2)	0.9031(2)	66(3)
C22	0.5139(3)	0.3028(2)	0.9241(2)	87(4)
C23	0.5753(3)	0.2604(2)	1.0069(2)	89(4)
C24	0.5747(3)	0.1631(2)	1.0687(2)	90(4)
C25	0.5127(3)	0.1082(2)	1.0477(2)	130(5)
C26	0.4512(3)	0.1506(2)	0.9649(2)	119(5)
C27	0.6370(7)	0.1181(4)	1.1608(4)	171(7)
C28	0.6777(8)	0.0053(5)	1.1887(6)	233(9)
C29	0.7293(13)	0.1583(9)	1.1519(10)	489(25)
C30	0.5736(14)	0.1457(12)	1.2342(7)	450(25)
C31	0.1686(3)	0.3775(2)	0.7053(3)	76(3)
C32	0.1445(3)	0.2850(2)	0.7558(3)	93(4)

Table 14. Positional Parameters (Å) for 6a (cont).

C33	0.0388(3)	0.2801(2)	0.7725(3)	94(4)
C34	-0.0429(3)	0.3677(2)	0.7386(3)	82(4)
C35	-0.0188(3)	0.4602(2)	0.6880(3)	90(5)
C36	0.0870(3)	0.4651(2)	0.6714(3)	84(4)
C37	-0.1581(5)	0.3648(7)	0.7607(6)	69(4)
C37	-0.2219(7)	0.4159(9)	0.6676(8)	109(7)
C39	-0.1731(8)	0.2572(9)	0.8014(12)	145(9)
C40	-0.1991(7)	0.4203(11)	0.8316(10)	116(7)
C41	0.1617(3)	0.3962(4)	0.9940(3)	95(4)
C42	0.2361(3)	0.3272(4)	1.0620(3)	81(4)
C43	0.2281(3)	0.2273(4)	1.1048(3)	87(4)
C44	0.1458(3)	0.1963(4)	1.0796(3)	104(4)
C45	0.0715(3)	0.2653(4)	1.0116(3)	126(5)
C46	0.0794(3)	0.3652(4)	0.9688(3)	126(5)
C47	0.1393(3)	0.0874(6)	1.1215(6)	146(7)
C48	0.1260(16)	0.0574(8)	1.2223(8)	802(39)
C49	0.2282(13)	0.0149(8)	1.1046(12)	380(21)
C50	0.0586(14)	0.0594(10)	1.0846(14)	369(23)
C51	0.1340(3)	0.6744(3)	0.7532(2)	80(4)
C52	0.0269(3)	0.6736(3)	0.7667(2)	85(4)
C53	-0.0417(3)	0.7164(3)	0.6887(2)	64(3)
C54	-0.0033(3)	0.7601(3)	0.5971(2)	87(4)
C55	0.1038(3)	0.7609(3)	0.5836(2)	113(5)
C56	0.1724(3)	0.7181(3)	0.6617(2)	88(4)
C57	-0.0797(7)	0.8112 (6)	0.5119(5)	150(6)
C58	-0.1102(10)	0.7247(8)	0.4898(8)	336(16)
C59	-0.1621(12)	0.8873(11)	0.5230(9)	462(23)
C60	-0.2190(11)	0.8450(10)	0.4147(7)	307(15)

Numbers in parentheses are estimated standard deviations in the least significant digits.

The form of the anisotropic thermal parameter is:

$$U = \exp[-2\pi^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3)$$

$$+ 2klbcU(2,3))\}]$$ where a, b, and c are reciprocal lattice constants

Figure Captions

Figure 1. ORTEP of $N_3P_3(p\text{-}OC_6H_4\text{-}CH_3)_6$ **(2a)**

Figure 2. ORTEP of $N_3P_3(p\text{-}OC_6H_4\text{-}OH)_6$ **(2b)**

Figure 3. ORTEP of $N_3P_3(p\text{-}OC_6H_4\text{-}OC_6H_4)_6$ **(2e)**

Figure 4. Unit cell packing diagram of $N_3P_3(p\text{-}OC_6H_4\text{-}OC_6H_4)_6$ **(2e)**

Figure 5. ORTEP of $N_3P_3(p\text{-}OC_6H_4\text{-}OCH_2C_6H_4)_6$ **(2f)**

Figure 6. Unit cell packing diagram of $N_3P_3(p\text{-}OC_6H_4\text{-}OCH_2C_6H_4)_6$ **(2f)**

Figure 7. ORTEP of $N_4P_4(p\text{-}OC_6H_4\text{-}OC_6H_4)_8$ **(4a)**

Figure 8. Unit cell packing arrangement of $N_4P_4(p\text{-}OC_6H_4\text{-}OC_6H_4)_8$ **(4a)**

$OP(O\text{-}C_6H_4\text{-}{}^tBu)_2NP(O\text{-}C_6H_4\text{-}{}^tBu)_3$ **(6a)**

Supplementary Material Table of Contents

Table S1. Summary of Characterization Data

Table S2. Summary of Crystal Data and Intensity Collection Parameters

Figure S3. ORTEP of $N_3P_3(p\text{-}OC_6H_4CH_3)_6$ **(2a)**

Table S4. Positional Parameters of $N_3P_3(p\text{-}OC_6H_4CH_3)_6$ **(2a)**

Table S5. Selected Bond Distances (Å) and Bond Angles (deg) for $N_3P_3(p\text{-}OC_6H_4CH_3)_6$ **(2a)**

Table S6 General Thermal Parameters for $N_3P_3(p\text{-}OC_6H_4CH_3)_6$ **(2a)**

Table S7. Structure Factor Tables for $N_3P_3(p\text{-}OC_6H_4CH_3)_6$ **(2a)**

Figure S8. ORTEP of $N_3P_3(p\text{-}OC_6H_4OH)_6$ **(2b)**

Table S9. Positional Parameters of $N_3P_3(p\text{-}OC_6H_4OH)_6$ **(2b)**

Table S10. Selected Bond Distances (Å) and Bond Angles (deg) for $N_3P_3(p\text{-}OC_6H_4OH)_6$ **(2b)**

Table S11 General Thermal Parameters for $N_3P_3(p\text{-}OC_6H_4OH)_6$ **(2b)**

Table S12. Structure Factor Tables for $N_3P_3(p\text{-}OC_6H_4OH)_6$ **(2b)**

Figure S13. ORTEP of $N_3P_3(p\text{-}OC_6H_4\text{-}OC_6H_5)_6$ **(2e)**

Table S14. Positional Parameters of $N_3P_3(p\text{-}OC_6H_4\text{-}OC_6H_5)_6$ **(2e)**

Table S15. Selected Bond Distances (Å) and Bond Angles (deg) of $N_3P_3(p\text{-}OC_6H_4\text{-}OC_6H_5)_6$ **(2e)**

Table S16. General Thermal Parameters for $N_3P_3(p\text{-}OC_6H_4\text{-}OC_6H_5)_6$

Table S17. Structure Factor Tables for $N_3P_3(p\text{-}OC_6H_4\text{-}OC_6H_5)_6$ **(2e)**

Figure S18. ORTEP of $N_3P_3(p\text{-}OC_6H_4\text{-}OCH_2C_6H_5)_6$ **(2f)**

Table S19. Positional Parameters of $N_3P_3(p\text{-}OC_6H_4\text{-}OCH_2C_6H_5)_6$ **(2f)**

Table S20. Selected Bond Distances (Å) and Bond Angles (deg) for $N_3P_3(p\text{-}OC_6H_4\text{-}OCH_2C_6H_5)_6$ **(2f)**

Table S21. General Thermal Parameters for $N_3P_3(p\text{-}OC_6H_4\text{-}OCH_2C_6H_5)_6$ **(2f)**

Table S22. Structure Factor Tables for $N_3P_3(p\text{-}OC_6H_4\text{-}OCH_2C_6H_5)_6$ **(2f)**

Table S23. ORTEP of $N_4P_4(p\text{-}OC_6H_4\text{-}OC_6H_5)_4$ **(4a)**

Table S24. Positional Parameters of $N_4P_4(p\text{-}OC_6H_4\text{-}OC_6H_5)_4$ **(4a)**

Table S25. Selected Bond Distances (Å) and Bond Angles (deg) of $N_4P_4(p\text{-}OC_6H_4\text{-}OC_6H_5)_4$ **(4a)**

Table S26. General Thermal Parameters for $N_4P_4(p\text{-}OC_6H_4\text{-}OC_6H_5)_4$ **(4a)**

Table S27. Structure Factor Tables for $N_4P_4(p\text{-}OC_6H_4\text{-}OC_6H_5)_4$ **(4a)**

Table S28. ORTEP of $OP(p\text{-}OC_6H_4\text{-}Bu^t)_2NP(p\text{-}OC_6H_4\text{-}Bu^t)_3$ **(6a)**

Table S29. Positional Parameters of $OP(p\text{-}OC_6H_4\text{-}Bu^t)_2NP(p\text{-}OC_6H_4\text{-}Bu^t)_3$ **(6a)**

Table S30. Selected Bond Distances (Å) and Bond Angles (deg) of $OP(p\text{-}OC_6H_4\text{-}Bu^t)_2NP(p\text{-}OC_6H_4\text{-}Bu^t)_3$ **(6a)**

Table S31. General Thermal Parameters for $OP(p\text{-}OC_6H_4\text{-}Bu^t)_2NP(p\text{-}OC_6H_4\text{-}Bu^t)_3$ **(6a)**

Table S32. Structure Factor Tables for $OP(p\text{-}OC_6H_4\text{-}Bu^t)_2NP(p\text{-}OC_6H_4\text{-}Bu^t)_3$ **(6a)**

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