The First Selective Cage Redistribution Reaction of P_4O_6[☆]

Stephan Strojek and Martin Jansen*

Institut für Anorganische Chemie der Universität,
Gerhard-Domagk-Str. 1, D-53121 Bonn, Germany

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Reaction of tetraphosphorus hexaoxide with organic azides leads selectively to the cage redistribution products **1** P_4O_6NPh, **2** $P_4O_6NC_2H_4Ph$, **3** $P_4O_6NSO_2CH_3$, **4** $P_4O_6NC_6H_{13}$, and **5** $P_4O_6NCO_2C_2H_5$ by nitrene insertion. The molecular structure consists of an adamantane-like P_4O_5N cage with a terminally bound oxygen atom. The P_4O_5N cagelike structure is confirmed by ^{31}P NMR spectroscopy and X-ray structure analysis. The P_4O_5N cages of the P_4O_6NR molecules possess a significant geometrical distortion.

Controlled cage redistribution reactions of P_4O_6 have always been of great interest in organophosphorus chemistry, because P_4O_6 could replace phosphorus trichloride as starting material in industrial chemistry. The use of the latter produces large amounts of undesirable ecologically harmful chlorine compounds, in particular hydrochloric acid which requires expensive recycling or waste management[1].

The known reactions of P_4O_6 usually result in the complete fragmentation of the P_4O_6 cage or lead to the formation of oxidation products while preserving the cagelike P_4O_6 structure[2−4]. Selective redistribution reactions involving the cage seem to be kinetically inhibited at low temperatures and uncontrollable at higher temperatures.

All the well-known oxidation products consist of an adamantane-like P_4O_6 cage with terminally bound chalcogen atoms (O, S, and Se). Attaching electron withdrawing substituents like oxygen, sulfur, and selenium terminally, results in characteristic geometrical distortions of the P_4O_6 cage which have been studied in some detail[5−11]. In general, the bonds extending from pentavalent phosphorus atoms are shorter than those extending from trivalent phosphorus atoms, and this distortion is felt throughout the whole molecule. As a consequence of attaching an electron-donating atom like nitrogen to phosphorus in P_4O_6, one would expect opposite geometrical distortions of the P_4O_6 cage, in agreement with quantum chemical calculations on $P_4O_6N^-$[12]. We have performed reactions of P_4O_6 with organic azides RN_3 (R = Ph, C_2H_4Ph, SO_2CH_3, C_6H_{13}, $CO_2C_2H_5$) for the purpose of synthesizing ions like $P_4O_6N^-$. These reactions evolve molecular nitrogen and lead to the first known examples of selective P_4O_6 cage redistribution products.

The reaction of P_4O_6 with organic azides is the first known example of a selective oxygen-nitrogen redistribution reaction that preserves the adamantane-like P_4O_6 cage structure and results in the cage redistribution products **1**−**5**. Using organic azides and P_4O_6 as starting materials, this reaction type is of general applicability. Selective insertion of the nitrene R−N leads to the formation of a P_4O_5N cage as a well-defined derivative of P_4O_6[13]. The exchanged bridging oxygen atom is found at a terminal position at one of the phosphorus atoms next to the new nitrogen bridge (Scheme 1). The inserted nitrogen atom causes characteristic geometrical distortions of the adamantane-like P_4O_6 cage structure. The insertion reaction of the nitrene R−N appears to take place only once. Our attempts to synthesize doubly substituted cage redistribution products of P_4O_6 have failed so far.

Scheme 1

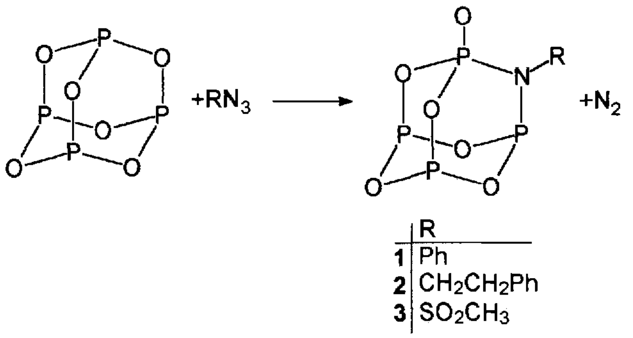
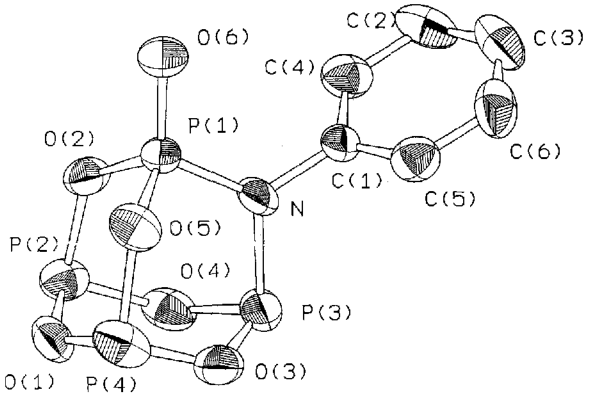


Figure 1. Molecular structure of **1** in the crystal (hydrogen atoms omitted). Selected bond lengths [pm][14] and angles [°]: P(1)−O(2) 158.4(2), P(1)−N 165.7(3), P(1)−O(6) 145.9(3), P(2)−O(2) 168.0(3), P(3)−N 173.0(3), P(3)−O(3) 163.8(3), P(4)−O(3) 160.6(3), N−C(1) 146.4(5), P(1)−N−C(1) 122.9(3), P(1)−N−P(3) 119.6(2), P(3)−N−C(1) 117.5(3), P(1)−O(2)−P(2) 125.6(2)



The molecules **1**−**3** consist of an adamantane-like P_4O_5N cage with one bridging nitrogen and one terminally bound oxygen atom (Figures 1−3). Calculations of best planes through N, P(1), P(3),

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Figure 2. Molecular structure of **2** in the crystal (hydrogen atoms omitted). Selected bond lengths [pm][14] and angles [°]: P(1)–O(2) 159.9(3), P(1)–N 167.3(3), P(1)–O(6) 147.0(3), P(2)–O(2) 165.5(3), P(3)–N 171.1(3), P(3)–O(4) 166.6(3), P(2)–O(4) 163.7(3), N–C(1) 150.5(5), P(1)–N–C(1) 121.5(3), P(1)–N–P(3) 119.7(2), P(3)–N–C(1) 117.8(3), P(1)–O(2)–P(2) 125.1(2)

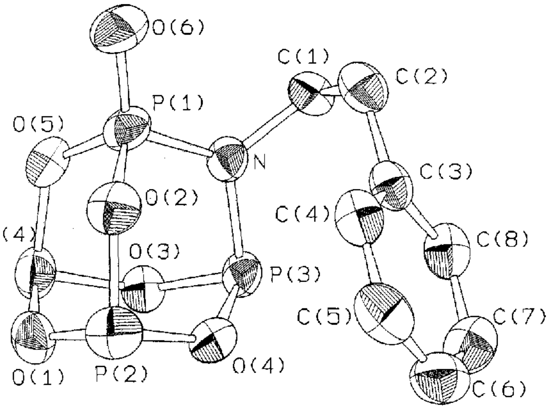
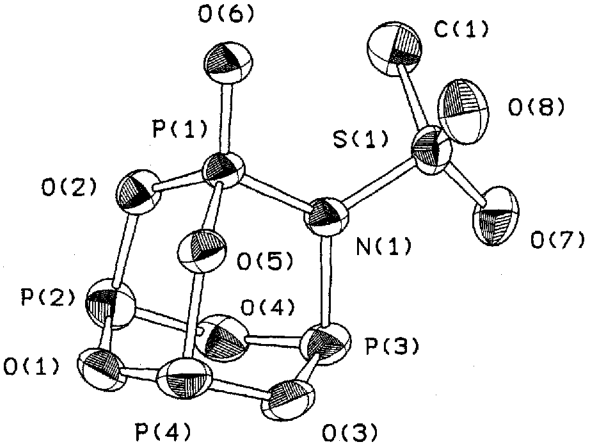


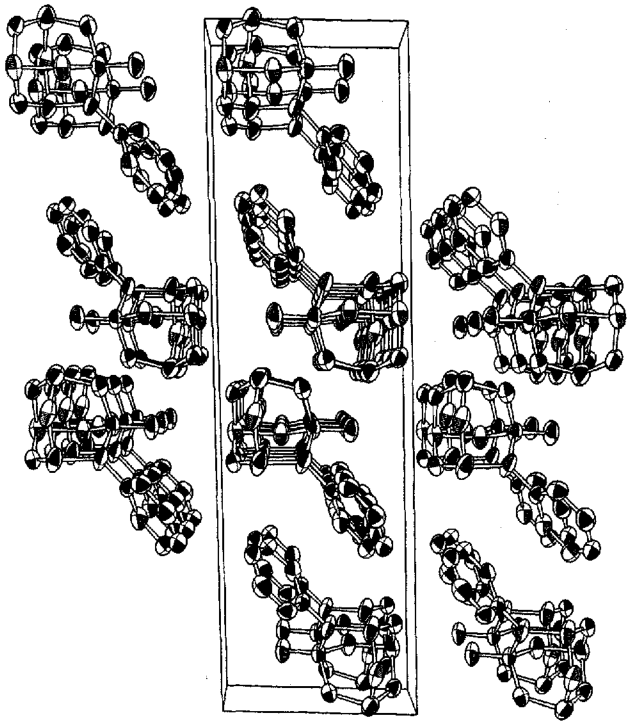
Figure 3. Molecular structure of **3** in the crystal (hydrogen atoms omitted). Selected bond lengths [pm][14] and angles [°]: P(1)–O(2) 156.8(4), P(1)–N 167.7(4), P(1)–O(6) 145.1(4), P(2)–O(2) 168.1(4), P(3)–N 178.4(4), P(3)–O(3) 164.6(4), P(4)–O(3) 163.9(4), N–S(1) 167.3(5), P(1)–N–S(1) 123.0(3), P(1)–N–P(3) 118.7(3), P(3)–N–S(1) 118.2(3), P(1)–O(2)–P(2) 126.1(2)



O(1), and O(6)[14] – ignoring the details of the organic substituents at the nitrogen atom – show that the P_4O_6N cage of the molecules belongs to the "pseudo point group" C_{2v} in the solid state, that is, the same group one would expect for the gaseous state. The general features of the molecular packing of **1**–**3** are exemplified by a plot of **1** (Figure 4). The molecules are arranged in columns which are densely packed following the principle of "dovetailing" (interlocking protrusions and hollows). Since van der Waals type forces dominate molecular packings, one would expect that the arrangement of the molecules is mainly determined by a tendency to fill the available space as effectively as possible[15]. In order to check whether this principle also applies in this case we have defined the "efficiency" of a molecular packing as the quotient between the volume of the molecule and the share of the volume of the unit cell available for one molecule. For the known derivatives of P_4O_6, with the exception of P_4O_{10}, efficiency values between 0.61 and 0.65 have been found[5]. The lower efficiency value of **1** and **2** (0.53 and 0.52; cf. Table 1) is obviously due to the rather extended phenyl or ethylphenyl groups attached to nitrogen.

The configuration around the nitrogen atom is essentially planar, for example for **1**: P(1)–N–C(1) 122.9°; P(1)–N–P(3) 119.5°; P(3)–N–C(1) 117.5°; sum of angles: 360° (for **2**: 359°; for **3**: 360°). In addition, the P–N bonds are shorter (168 pm on average) than one would expect for a covalent phosphorus nitrogen single bond (177 pm).

Figure 4. Molecular packing of **1** in the crystal



The trends in bond angles at the oxygen and nitrogen atoms [P(1)–O(5)–P(4) 125.2°; P(1)–N–P(3) 119.5°, respectively, **1**] agree with those predicted by the VSEPR concept. The dihedral angle between the mirror plane of the P_4O_5N cage [N, P(1), P(3), O(1), O(6)] and the ring plane of the phenyl group is 106.2° for **1** and 51.0° for **2**. The deviation from a 90° or 180° angle, which would result in a higher symmetry of the molecules, is certainly a result of the molecular packing in the solid state.

The molecular structures of **1**–**3**, P_4O_7, P_4O_6S, and P_4O_6Se show similar geometrical distortions of their adamantane-like cage structures due to the addition of terminally bound chalcogen atoms. There are three different types of P–O linkages in the molecules (see Table 1)[5,11]. These show considerable variations in their lengths. The distortion of the molecular cage structure is reflected most clearly by the P(V)–O and P(V)–N distances. In all cases, the P–O and P–N bonds extending from the pentavalent phosphorus atoms are significantly shorter than those extending from the trivalent phosphorus atoms (see Table 1 and Figures 1–3)[5]. The molecular cage structures of **1**–**3** and P_4O_7 are similar even in the details of their bond lengths and angles. In general, an additional distortion of the P_4O_5N cage of **1**–**3**, in comparison with P_4O_7, is introduced by the greater covalent radius of nitrogen as compared to oxygen. Accordingly, the P(III)–N bond in the case of **3** is 8.0 pm longer (176.0; **1**: 172.9; **2**: 171.1) than the related P(III)–O bond of P_4O_7 (168.0). Another effect of the substitution of the nitrogen for oxygen within the cage is the slight elongation of the P(3)–O(3) and P(3)–O(4) bonds (e.g. **1**: 164.7, **2**: 165.8, **3**: 164.6) over the P(2)–O(4) and P(4)–O(3) bonds (e.g. **1**: 162.4, **2**: 163.5, **3**: 163.9.) According to quantum chemical calculations, this effect is expected to occur similarly in the $P_4O_6N^-$ anion[12].

Table 1. Comparison of bond lengths and packing of P_4O_6 derivatives

	1	**2**	**3**	P_4O_7[5]	P_4O_6S[5]	P_4O_6Se[11]
P(V)–O, S, Se	158.5(3)	159.1(6)	157.4(5)	159.0(8)	159.6(2)	159.4(4)
P(III)–O[–P(V)]	167.7(3)	166.0(7)	166.3(5)	168.0(6)	167.8(2)	168.4(4)
P(III)–O[–P(III)]	162.2(3)	163.8(7)	162.9(5)	164.0(9)	163.7(2)	164.6(4)
Volume of the molecule [Å^3]	145.1	168.2	142.1	103.5	117.2	123.7
Volume of the unit cell/Z [Å^3]	273.4	326.7	239.9	166.3	189.5	190.8
Efficiency	0.53	0.52	0.59	0.62	0.62	0.65

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Experimental

The experiments were performed under purified dry argon using standard Schlenk techniques. Solvents were purified, dried, and distilled under argon. P_4O_6 (Hoechst AG, Knapsack) was freshly distilled in vacuo before use. ^{31}P NMR: Bruker AMX 300; IR: Bruker IFS 113v.

9-Phenyl-2,4,6,8,10-pentaoxa-9-aza-1,3,5,7-tetraphosphatricyclo[3.3.1.1^{3,7}]decane 1-Oxide (**1**): A solution of 0.7 g (3.2 mmol) P_4O_6 and 0.6 g (5.0 mmol) phenyl azide[16] in 20 ml toluene was refluxed for 5 h. After evaporation of the solvent, the residue was sublimed in vacuo – first 70 °C to –25 °C, secondly 70 °C to room temperature – resulting in colourless crystals of **1**. Yield 0.4 g (43%). – ^{31}P NMR (toluene, H_3PO_4 ext.): δ [P(2)/P(4)] = 140.2 [d, –P(3), J = 50.8 Hz], δ [P(3)] = 136.9 [t, –P(2)/P(4), J = 50.8 Hz], δ [P(1)] = –43.1. – IR (cm^{-1}): ν(C–H) 2924, ν(C–C) 1591, 1487, ν_{as}(P–O) 974. – $C_6H_5NO_6P_4$ (311.0): calcd. C 24.17, H 1.77, N 4.49, P 39.87; found C 24.50, H 2.08, N 3.97, P 39.51.

9-(2-Phenylethyl)-2,4,6,8,10-pentaoxa-9-aza-1,3,5,7-tetraphosphatricyclo[3.3.1.1^{3,7}]decane 1-Oxide (**2**): A solution of 0.7 g (3.3 mmol) P_4O_6 and 0.7 g (5 mmol) phenylethyl azide[17] in 20 ml toluene is refluxed for 10 h. After evaporation of the solvent, the residue is sublimed in vacuo – first 65 °C to –25 °C, secondly 65 °C to room temperature – resulting in colourless crystals of **2**. Yield 0.2 g (18%). – ^{31}P NMR (toluene, H_3PO_4 ext.): δ [P(2)/P(4)] = 142.7 (d, –P(3), J = 48.3 Hz), δ [P(3)] = 145.7 (t, –P(2)/P(4), J = 48.3 Hz), δ [P(1)] = –39.3. – $C_8H_9NO_6P_4$ (338.9): calcd. C 28.35, H 2.66, N 4.13, P 36.55; found C 28.05, H 2.77, N 4.40, P 36.38.

9-(Methylsulfonyl)-2,4,6,8,10-pentaoxa-9-aza-1,3,5,7-tetraphosphatricyclo[3.3.1.1^{3,7}]decane 1-Oxide (**3**): A solution of 0.7 g (3.3 mmol) P_4O_6 and 0.6 g (5 mmol) methylsulfonyl azide[18] in 20 ml toluene is refluxed for 6 h. After evaporation of the solvent, the residue is sublimed in vacuo – first 65 °C to –25 °C, secondly 65 °C to room temperature – resulting in colourless crystals of **3**. Yield 0.35 g (34%). ^{31}P NMR (toluene, H_3PO_4 ext.): δ [P(2)/P(4)] = 132.0 (d, –P(3), J = 55.7 Hz), δ [P(3)] = 117.4 (t, –P(2)/P(4), J = 55.7 Hz), δ = [P(1)] = –47.0. – IR (cm^{-1}) = ν(C–H) 3034, 2934, ν(S–O) 1366, 1168, ν_{as}(P–O) 958. – $CH_3NO_8P_4S$ (312.88): calcd. C 3.84, H 0.96, N 4.47, P 39.59; found C 3.78, H 1.05, N 4.23, P 39.30.

X-Ray Structural Analysis: The structures were solved by direct methods and refined by full matrix least squares against F^2. Crystal structure and numerical data for the structure determination are given in Table 2[20].

Table 2. Crystallographic data for **1**–**3**

	1	**2**	**3**
Formula	$C_6H_5NO_6P_4$	$C_8H_9NO_6P_4$	$CH_3NO_8P_4S$
Mol. mass	311.00	338.91	312.88
Cryst. size	0.5 × 0.3 × 0.1	0.5 × 0.2 × 0.1	0.3 × 0.3 × 0.1
Cryst. system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/a$
a [pm]	712.4(2)[a]/ 712.9(1)[b]	672.8(1)[a]	1457.6(5)[a]/ 1454.1(2)[b]
b [pm]	635.9(1)/636.6(1)	1525.3(7)	941.5(3)/939.3(2)
c [pm]	2415.8(5)/ 2415.6(4)	1303.2(3)	1522.4(5)/ 1518.5(3)
β [°]	92.01(1)/91.98(1)	102.30(1)	112.31(3)/ 112.31(2)
V [$\times 10^6$ pm^3]	1093.6	1306.7	1918.8
Z	4	4	8
$d_{calcd.}$ [g cm^{-3}]	1.885	1.723	2.167
Diffractometer		Enraf Nonius CAD 4	
Radiation (Graphite-monochromated)		Mo-K_α	
T [K]		296	
μ [mm^{-1}]	0.70	0.60	1.03
Scan method		ω-θ	
2θ (max) [°]	49.9	50.1	46.1
Total no. of reflexions	3273	5452	6253
No. of unique reflexions	1692	2299	2676
No. of observed reflexions [$F_o > 4\sigma(F_o)$]	1408	1561	1911
No. of refined parameters	170	173	290
GOF (F^2)	1.122	1.164	1.102
R_1	0.042	0.042	0.042
wR^2[19]	0.114	0.113	0.113
Residual electron density [e Å^{-3}]	0.75, –0.66	0.31, –0.34	0.86, –0.37

[a] CAD 4 data. – [b] Powder diffraction data.

☆ Dedicated to Professor *Rolf Appel* on the occasion of his 75th birthday.

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