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Structure, Bonding, and Chemistry of *closo*-Tetraphosphorus Hexakis(methylimide), $P_4(NCH_3)_6$, and Its Derivatives. 1. The Structures of the Tetra-*P*-thio and Tetra-*P*-oxo Derivatives

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The title compounds, which both contain molecules with virtual T_d symmetry, have been studied by X-ray crystallography. In $O_4P_4(NMe)_6$ there are four crystallographically independent molecules in the asymmetric unit. The space group is $P2_1$ with $a = 15.219$ (6) Å, $b = 14.831$ (5) Å, $c = 13.218$ (3) Å, $\beta = 92.97$ (3)°, $V = 2979$ (2) Å^3, and $Z = 8$. The structure was solved using direct methods followed by difference maps and eventually refined to $R_1 = 0.061$ and $R_2 = 0.083$ using 3834 reflections with $I > 3\sigma(I)$. Both enantiomorphs of the polar space group were tested and gave indistinguishable results. The molecular dimensions, averaged over four molecules assuming T_d symmetry in each one, are P–O = 1.45 (1) Å, P–N, = 1.67 (2) Å, P–P = 2.88 (1) Å, N–C = 1.52 (5) Å, P–N–P = 119.2 (13)°, N–P–N = 104.1 (15)°, P–N–C = 116 (3)°, and N–P–O = 114.4 (11)°. The configurations about nitrogen are planar within the errors. In $S_4P_4(NMe)_6$ using data collected at 3 °C the space group is $P\bar{4}2_1c$ and the unit cell dimensions are $a = 9.486$ (2) Å, $c = 9.884$ (4) Å, $V = 889.5$ (2) Å^3, and $Z = 2$. The average molecular dimensions are P–S = 1.912 (24) Å, P–N = 1.656 (14) Å, C–N = 1.47 (3) Å, P–P = 2.89 (3) Å, P–N–P = 120.6 (5)°, N–P–N = 103 (2)°, P–N–C = 119 (1)°, and N–P–S = 116 (4)°. Certain crystallographic problems due to disorder, crystal plasticity, or high thermal motion are discussed. These structures are discussed in comparison with that of the parent compound, $P_4(NMe)_6$, and possible causes of the small changes in certain distances and angles are considered.

Introduction

As a part of a continuing study of *closo*-*N*-methylphosphoramide, $P_4(NMe)_6$, and its derivatives, e.g., $X_nP_4(NMe)_6$, where $n = 1$–4 and X may be O, S, or a Lewis acid, we have investigated the effect of attaching the addends X upon the structure of the $P_4(NMe)_6$ core. We have previously given a brief report on the structure and photoelectron spectrum of $P_4(NMe)_6$ itself.[2] We now present the results of a structural study of two limiting members of these series, $O_4P_4(NMe)_6$ and $S_4P_4(NMe)_6$. The preparations and some chemical properties of each of these have been described earlier.[3-5] While this work was in progress, an X-ray crystallographic study of $S_4P_4(NMe)_6$ was reported, but the results were relatively inaccurate and the present ones, though still leaving much to be desired, represent a significant improvement. In later papers we shall report the structures of $SP_4(NMe)_6$, $S_2P_4(NMe)_6$, and $S_3P_4(NMe)_6$, spectroscopic studies of the $S_4P_4(NMe)_6$ and $O_4P_4(NMe)_6$ compounds, and additional adducts of $P_4(NMe)_6$.

Experimental Section

Both compounds were prepared by methods previously described.[3-5]

$O_4P_4(NMe)_6$. X-ray Data Collection. The crystal selected had approximate dimensions of 0.3 × 0.3 × 0.4 mm; it was mounted in paraffin in a glass capillary tube. Data were collected at 21 ± 1 °C on a Syntex $P\bar{1}$ automated diffractometer using Mo Kα radiation monochromatized with a graphite crystal in the incident beam. The automatic centering and indexing procedures followed have been described elsewhere.[6] Preliminary photographs revealed monoclinic symmetry. The systematic absence ($0k0$, $k \neq 2n$) indicated $P2_1$ and $P2_1/m$ as possible space groups. The principal crystallographic data are as follows: $a = 15.219$ (6) Å, $b = 14.831$ (5) Å, $c = 13.218$ (3) Å, $\beta = 92.97$ (3)°, $V = 2979$ (2) Å^3, $d_{calcd} = 1.615$ g/cm^3 for $Z = 8$ and a molecular weight of 362.14.

A total of 5514 unique reflections with $0° < 2\theta \leq 50°$ were collected using the θ–2θ scan technique, variable scan rates from 4.0 to 24.0°/min, and a scan range from 2θ(Mo Kα_1) − 1.0° to 2θ(Mo Kα_2) + 1.0°. The intensities of three standard reflections measured after every 100 reflections showed no significant variation during data collection. The data were corrected for Lorentz and polarization effects, but an absorption correction was deemed unnecessary (linear absorption coefficient $\mu = 5.31$ cm^{-1}).

$O_4P_4(NMe)_6$. Solution and Refinement of the Structure.[7] Attempts at structure solution in the space group $P2_1/m$ were not successful. Working in the noncentrosymmetric space group $P2_1$ (No. 4), all phosphorus atoms, twelve nitrogen atoms, and one oxygen atom were located from an E map. This map was generated using as a starting phase set the one with the highest figure of merit produced by the program MULTAN operating on an input of the 426 reflections with E values greater than 1.75. These positions were used to phase a Fourier difference map, from which the remaining nonhydrogen atoms were located. Three cycles of least-squares refinement of a scale factor, all variable positional parameters (the y value of P(1) was fixed to define the origin), and isotropic temperature factors gave discrepancy indices

$$R_1 = \sum||F_o| - |F_c||/|F_o| = 0.084$$

$$R_2 = [\sum w(||F_o| - |F_c||)^2/\sum w|F_o|^2]^{1/2} = 0.113$$

Only those 3834 reflections with $F_o^2 \geq 3\sigma(F_o^2)$ were included in the refinement. Atomic scattering factors were from ref 8 for neutral atoms, and anomalous scattering terms[9] were included for all atoms. The function minimized during all least-squares refinements was $\sum w(|F_o| - |F_c|)^2$, where the weighting factor is $w = 4F_o^2/\sigma(F_o^2)^2$. A value of 0.07 was used for p in the calculation of σ.

Anisotropic temperature factors were refined for the phosphorus, nitrogen, and oxygen atoms. Due to the large number of parameters at this stage (601), it was not convenient to refine the entire structure at once. Therefore half the atoms (two complete molecules) were refined in each least-squares cycle, alternating molecules refined after each cycle. After eight such half-cycles, the largest parameter shift was 0.31 times the estimated standard deviation and $R_1 = 0.061$ and $R_2 = 0.083$. The esd of an observation of unit weight was 1.686. A final Fourier difference map contained only peaks due to hydrogen atoms. Tables of observed and calculated structure factors are available as supplementary material.

In order to determine the correct enantiomorph for the structure, refinement was carried out with the signs of the $\Delta f''$ terms of the atoms reversed. Although some small parameter shifts occurred (generally less than one esd), the discrepancy indices did not change, nor did the calculated structure factors look appreciably different. Thus, though it was not possible to determine the correct enantiomorphic configuration, it appears that either one carries the same structural information.

$S_4P_4(NMe)_6$. Data Collection. A crystal of approximate dimensions 0.45 × 0.30 × 0.35 mm was sealed in a glass capillary. The crystal was found to have Laue symmetry $4/mmm$ and systematic absences were consistent with the space group $P\bar{4}2_1c$. Unit cell dimensions, measured using accurately centered reflections in the range 18° < Mo Kα < 30° at 22 ± 1 and 3 ± 1 °C, respectively, were as follows: $a = 9.498$ (2), 9.486 (2) Å; $c = 9.883$ (2), 9.884 (4) Å; $V = 891.6$ (2), 889.5 (2) Å^3. The volume is as expected for $Z = 2$. The intensity data were also recorded at both 22 ± 1 and 3 ± 1 °C using the θ–2θ scans with the range from 0.9° below Mo Kα_1 to 0.9° above Mo Kα_2.

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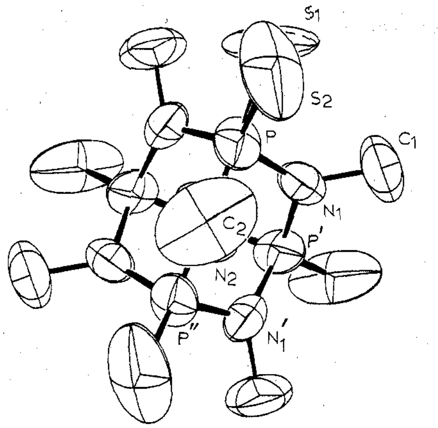

Figure 1. A view of the $S_4P_4(NMe)_6$ molecule looking down along the crystallographic $\bar{4}$ axis. The two sulfur atoms, S(1) and S(2) refined with the 3 °C data, are shown on the P atom only; on the other phosphorus atoms only S(2) is shown to avoid overcrowding the picture.

Scan times were varied from 4 to 24°/min at 3 °C but were fixed at 2°/min for $2\theta \leq 55°$ and 1°/min for $55° < 2\theta \leq 62.1°$. Standard reflections checked at intervals of 150 data points showed only random variations of ±3%. At each temperature, data were collected in the range $0° < 2\theta \leq 55°$. For the 22 °C data a total of 893 reflections were counted of which 347 with $I > 3\sigma(I)$ were retained as observed, while at 3 °C the corresponding numbers were 517 and 293. The smaller number of observed reflections in the latter case appears to be attributable to poorer crystal quality.

$S_4P_4(NMe)_6$. Solution and Refinement—3 °C Data. Initial positional parameters were those reported by Cordes.[10] When the refinement of positional parameters first employing isotropic and subsequently anisotropic thermal parameters resulted in $R_1 > 11.0\%$ and large thermal parameters for the sulfur atom, a model involving disordered sulfur atoms was investigated. A difference Fourier map following a structure factor calculation excluding the sulfur atoms revealed two positions of approximately equal peak heights for the sulfur atoms. Refinement of the occupancy factors for these two sulfur atoms converged to essential equality, and the occupancy factors were fixed at 50% for the final refinement. Attempts to deduce a disordered model for all atoms in the structure were unsuccessful. The final anisotropic discrepancy indices were $R_1 = 0.083$ and $R_2 = 0.106$, and no parameter shifted in the last cycle by more than 0.08 of its esd.

$S_4P_4(NMe)_6$. Solution and Refinement—22 °C Data. Identical procedures were followed for refinement of the data collected at 22 °C as were used for the data collected at 3 °C. However, a difference Fourier map revealed three likely sulfur positions with their peak heights in the approximate ratios 50:35:15. During the least-squares refinements, the occupancy factors for S(1) and S(2) were refined and the atom multiplier of S(3) was set equal to 1 minus the sum of the occupancies for S(1) and S(2). Final occupancy factors for S(1), S(2), and S(2) are 0.652 (5), 0.278 (5), and 0.070, respectively. In the final cycle of anisotropic refinement $R_1 = 0.092$ and $R_2 = 0.119$, and the largest shift in any parameter was 0.3 times its esd.

Results

The atomic positional and thermal parameters for each compound are presented in Tables I and II.

Tables listing all individual bond distances and angles for $O_4P_4(NMe)_6$ and $S_4P_4(NMe)_6$, are available as supplementary material. Table III gives average values of distances and angles from both the 3 °C and the 22 °C data sets and from the results previously given by Hunter and Cordes.[10]

Figures 1 and 2 present two views of the $S_4P_4(NMe)_6$ molecule, as given by the 3 °C data, and show the nature of the ambiguity regarding the positions of the sulfur atom. Figure 3 gives an ORTEP drawing of one of the $O_4P_4(NMe)_6$ molecules and Figure 4 is a stereoview of the unit cell.

Discussion

Our studies of $P_4(NMe)_6$ and its derivatives have been motivated by the desire to evaluate the degree of N–P π bonding, and hence the extent to which global (as opposed to merely linear or cyclic) delocalization of π electrons exists in these molecules and how much it varies from one to another. From a structural point of view the extent of P–N π bonding will be directly evidenced, if at all, only in the P–N bond distances. Therefore, in the following discussion attention will be focused entirely on this parameter in each compound.

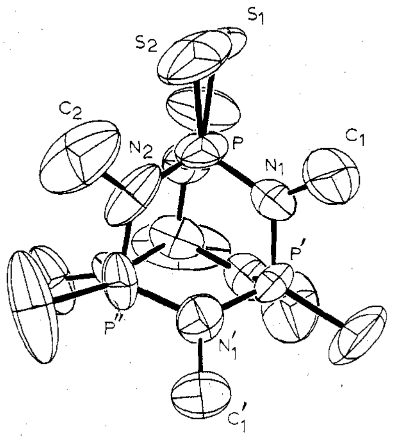

Figure 2. View of the $S_4P_4(NMe)_6$ molecule approximately along the molecular (but not crystallographic) threefold axis. Both S(1) and S(2) used in refining the 3 °C data are shown on the phosphorus atom P, but, for the sake of clarity, only S(2) is shown on the other three phosphorus atoms.

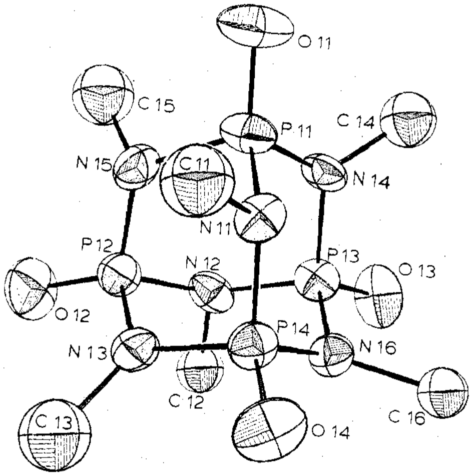

Figure 3. ORTEP drawing of one of the crystallographically independent $O_4P_4(NMe)_6$ molecules. All atom numbers begin with 1; in the other three molecules numbers are in analogous sets beginning with 2, 3, and 4.

The two structures reported here suffer from the same lack of precision as did that of $P_4(NMe)_6$. The crystals of $P_4(NMe)_6$ contain two molecules in the asymmetric unit so that there are 24 crystallographically independent P–N distances. Ordinarily, one might expect that this would lead to a very accurate evaluation of the P–N bond length, since there are so many separate measurements of what would be expected, on chemical grounds, to be the same quantity. Unfortunately, the results of the different measurements are spread over such a large range that the average value carries a large uncertainty interval.[11] Thus, as shown in Figure 5, for $P_4(NMe)_6$, the 24 P–N distances range from 1.65 to 1.74 Å. Even neglecting the two extreme ones, the range is from 1.68 to 1.72 Å so that the average value of 1.695 Å has an uncertainty of 0.012 Å.

The same difficulty has arisen in both the $S_4P_4(NMe)_6$ and $O_4P_4(NMe)_6$ cases, as shown by their histograms in Figure 5. There is, as discussed in detail in the Experimental Section, a gross disorder of a puzzling character in the former, and the

Table I. Positional and Anisotropic Thermal Parameters[a,b] for $O_4P_4(NMe)_6$

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P(11)	0.6457 (2)	0.5586 (0)	0.0472 (2)	0.0046 (2)	0.0031 (1)	0.0051 (2)	−0.0019 (3)	0.0021 (3)	0.0001 (3)
P(12)	0.8053 (2)	0.6667 (2)	0.0487 (2)	0.0027 (1)	0.0034 (1)	0.0060 (2)	0.0009 (2)	−0.0003 (3)	−0.0007 (3)
P(13)	0.3190 (2)	0.1730 (2)	0.1216 (2)	0.0038 (1)	0.0040 (1)	0.0037 (2)	0.0007 (3)	0.0016 (2)	−0.0005 (3)
P(14)	0.6379 (2)	0.7526 (2)	0.0688 (2)	0.0028 (1)	0.0032 (1)	0.0045 (2)	0.0006 (2)	0.0011 (2)	0.0001 (3)
P(21)	0.1520 (2)	0.5610 (2)	0.0420 (2)	0.0050 (2)	0.0026 (1)	0.0039 (2)	−0.0006 (3)	0.0005 (3)	0.0010 (3)
P(22)	0.8762 (2)	0.2097 (2)	0.0964 (2)	0.0030 (1)	0.0031 (1)	0.0035 (1)	−0.0010 (2)	−0.0006 (2)	−0.0006 (2)
P(23)	0.7014 (2)	0.1439 (2)	0.0541 (2)	0.0027 (1)	0.0029 (1)	0.0037 (1)	−0.0010 (2)	0.0001 (2)	0.0015 (2)
P(24)	0.2094 (2)	0.7407 (2)	0.0987 (2)	0.0026 (1)	0.0035 (1)	0.0040 (2)	−0.0006 (2)	0.0002 (2)	−0.0027 (3)
P(31)	0.6015 (2)	0.0908 (2)	0.4615 (2)	0.0047 (2)	0.0025 (1)	0.0043 (2)	−0.0007 (3)	0.0011 (3)	0.0009 (3)
P(32)	0.4450 (2)	0.9837 (2)	0.4638 (2)	0.0029 (1)	0.0037 (1)	0.0044 (2)	0.0012 (2)	−0.0015 (2)	−0.0009 (3)
P(33)	0.4288 (2)	0.4805 (2)	0.3667 (2)	0.0027 (1)	0.0037 (1)	0.0030 (1)	0.0005 (2)	0.0001 (2)	0.0000 (3)
P(34)	0.6120 (2)	0.8971 (2)	0.4447 (2)	0.0031 (1)	0.0025 (1)	0.0044 (2)	0.0010 (2)	0.0015 (2)	−0.0002 (3)
P(41)	0.0956 (2)	0.1016 (2)	0.4363 (2)	0.0041 (1)	0.0026 (1)	0.0051 (2)	−0.0002 (2)	−0.0004 (3)	0.0008 (3)
P(42)	0.8750 (2)	0.4544 (2)	0.4237 (2)	0.0031 (1)	0.0039 (2)	0.0048 (2)	−0.0010 (2)	−0.0001 (3)	−0.0018 (3)
P(43)	0.0483 (2)	0.9223 (2)	0.3761 (2)	0.0026 (1)	0.0034 (1)	0.0041 (2)	0.0003 (2)	0.0018 (2)	−0.0015 (3)
P(44)	0.0511 (2)	0.5143 (2)	0.4758 (2)	0.0030 (1)	0.0035 (1)	0.0037 (2)	−0.0021 (2)	0.0012 (2)	0.0000 (3)
O(11)	0.6118 (6)	0.4727 (6)	0.0798 (7)	0.0055 (4)	0.0034 (4)	0.0109 (7)	−0.0017 (8)	0.0063 (9)	0.0007 (10)
O(12)	0.8998 (5)	0.6712 (7)	0.0776 (8)	0.0031 (4)	0.0075 (6)	0.0110 (8)	0.0018 (9)	−0.0016 (9)	−0.0014 (13)
O(13)	0.3302 (6)	0.1822 (7)	0.2304 (6)	0.0049 (4)	0.0091 (7)	0.0035 (4)	−0.0000 (9)	0.0017 (7)	0.0014 (10)
O(14)	0.5931 (5)	0.8250 (6)	0.1166 (6)	0.0046 (4)	0.0046 (4)	0.0062 (5)	0.0027 (7)	0.0048 (7)	−0.0003 (8)
O(21)	0.1156 (6)	0.4764 (6)	0.0787 (6)	0.0051 (4)	0.0040 (4)	0.0079 (6)	−0.0026 (8)	0.0033 (8)	0.0015 (9)
O(22)	0.9373 (6)	0.2477 (6)	0.1738 (6)	0.0046 (4)	0.0063 (5)	0.0054 (5)	−0.0040 (8)	−0.0002 (8)	−0.0045 (9)
O(23)	0.6156 (5)	0.1302 (6)	0.0943 (6)	0.0034 (4)	0.0046 (4)	0.0064 (5)	−0.0011 (7)	0.0009 (7)	0.0029 (9)
O(24)	0.2184 (6)	0.8064 (6)	0.1819 (6)	0.0047 (4)	0.0056 (5)	0.0060 (5)	0.0003 (8)	0.0009 (8)	−0.0057 (9)
O(31)	0.6379 (7)	0.1763 (6)	0.4294 (7)	0.0104 (7)	0.0037 (4)	0.0062 (6)	−0.0036 (10)	0.0004 (10)	0.0027 (9)
O(32)	0.3517 (5)	0.9803 (6)	0.4317 (6)	0.0035 (4)	0.0052 (5)	0.0077 (6)	0.0000 (8)	−0.0018 (8)	−0.0003 (10)
O(33)	0.4152 (5)	0.4729 (6)	0.2570 (5)	0.0043 (4)	0.0058 (5)	0.0029 (4)	−0.0003 (8)	−0.0006 (7)	−0.0019 (8)
O(34)	0.6564 (6)	0.8227 (6)	0.3958 (6)	0.0054 (4)	0.0037 (4)	0.0063 (5)	0.0013 (8)	0.0001 (8)	−0.0007 (8)
O(41)	0.1287 (7)	0.1876 (6)	0.4043 (8)	0.0098 (7)	0.0032 (5)	0.0099 (7)	−0.0006 (10)	0.0032 (12)	0.0019 (10)
O(42)	0.8171 (6)	0.4217 (7)	0.3425 (6)	0.0042 (4)	0.0070 (5)	0.0064 (5)	−0.0000 (9)	−0.0015 (8)	−0.0047 (10)
O(43)	0.0401 (6)	0.8601 (6)	0.2924 (6)	0.0056 (4)	0.0046 (5)	0.0064 (5)	−0.0017 (8)	0.0026 (8)	−0.0043 (8)
O(44)	0.1391 (5)	0.5259 (6)	0.4389 (6)	0.0045 (4)	0.0060 (5)	0.0055 (5)	−0.0032 (8)	0.0027 (8)	0.0007 (9)
N(11)	0.6046 (6)	0.6511 (6)	0.0987 (6)	0.0030 (4)	0.0036 (5)	0.0039 (5)	0.0006 (8)	0.0017 (7)	0.0011 (9)
N(12)	0.2173 (6)	0.1766 (7)	0.0762 (7)	0.0033 (4)	0.0036 (5)	0.0052 (6)	0.0006 (8)	0.0014 (8)	0.0027 (9)
N(13)	0.7475 (6)	0.7468 (6)	0.0982 (7)	0.0030 (4)	0.0027 (4)	0.0060 (6)	0.0013 (8)	−0.0005 (8)	−0.0004 (9)
N(14)	0.3599 (6)	0.0768 (6)	0.0771 (6)	0.0043 (4)	0.0026 (4)	0.0039 (5)	0.0017 (8)	−0.0005 (8)	0.0018 (8)
N(15)	0.7587 (6)	0.5730 (6)	0.0769 (7)	0.0042 (5)	0.0032 (5)	0.0058 (6)	0.0024 (8)	−0.0009 (9)	0.0002 (9)
N(16)	0.3676 (6)	0.2548 (6)	0.0563 (7)	0.0032 (4)	0.0031 (4)	0.0047 (5)	0.0003 (8)	0.0001 (8)	−0.0013 (9)
N(21)	0.1399 (5)	0.7765 (6)	0.0039 (7)	0.0029 (4)	0.0020 (4)	0.0052 (6)	−0.0001 (7)	−0.0005 (8)	−0.0012 (8)
N(22)	0.2522 (6)	0.5527 (6)	−0.0083 (6)	0.0036 (5)	0.0026 (4)	0.0042 (5)	0.0022 (8)	−0.0009 (8)	0.0003 (8)
N(23)	0.1652 (6)	0.6419 (6)	0.1318 (6)	0.0038 (4)	0.0029 (4)	0.0041 (5)	−0.0003 (8)	0.0007 (8)	0.0001 (9)
N(24)	0.7770 (6)	0.1880 (6)	0.1342 (6)	0.0031 (4)	0.0028 (4)	0.0033 (5)	−0.0005 (7)	−0.0002 (7)	−0.0006 (8)
N(25)	0.3002 (5)	0.7166 (7)	0.0443 (7)	0.0023 (4)	0.0040 (5)	0.0054 (5)	−0.0006 (8)	−0.0001 (8)	−0.0035 (9)
N(26)	0.9101 (6)	0.1101 (6)	0.0504 (6)	0.0028 (4)	0.0029 (4)	0.0040 (5)	0.0004 (7)	−0.0017 (8)	−0.0012 (8)
N(31)	0.3782 (5)	0.3989 (6)	0.4287 (6)	0.0016 (3)	0.0031 (4)	0.0043 (5)	−0.0004 (7)	0.0005 (7)	−0.0025 (8)
N(32)	0.6511 (6)	0.9993 (7)	0.4141 (6)	0.0045 (5)	0.0041 (5)	0.0030 (5)	−0.0001 (8)	0.0020 (8)	−0.0011 (9)
N(33)	0.4992 (7)	0.0787 (6)	0.4337 (7)	0.0056 (5)	0.0034 (5)	0.0038 (5)	0.0021 (9)	−0.0003 (9)	−0.0004 (9)
N(34)	0.5335 (6)	0.4762 (6)	0.4089 (6)	0.0029 (4)	0.0033 (4)	0.0042 (5)	0.0004 (8)	0.0009 (7)	−0.0013 (9)
N(35)	0.3917 (6)	0.5750 (6)	0.4146 (7)	0.0030 (4)	0.0039 (5)	0.0050 (6)	0.0037 (8)	0.0011 (8)	0.0003 (9)
N(36)	0.5035 (6)	0.9001 (6)	0.4148 (6)	0.0040 (4)	0.0026 (4)	0.0043 (5)	−0.0008 (8)	−0.0028 (8)	−0.0026 (8)
N(41)	0.8465 (6)	0.5531 (6)	0.4681 (6)	0.0038 (4)	0.0036 (5)	0.0035 (5)	−0.0010 (8)	−0.0016 (8)	0.0002 (9)
N(42)	0.9505 (5)	0.9437 (6)	0.4267 (6)	0.0022 (4)	0.0034 (4)	0.0044 (5)	0.0008 (7)	0.0004 (7)	−0.0013 (8)
N(43)	0.0851 (6)	0.0252 (6)	0.3476 (6)	0.0032 (4)	0.0043 (5)	0.0035 (5)	−0.0008 (8)	0.0021 (8)	0.0004 (9)
N(44)	0.9771 (7)	0.4738 (7)	0.3888 (6)	0.0054 (5)	0.0044 (5)	0.0032 (5)	−0.0021 (9)	−0.0008 (9)	−0.0009 (9)
N(45)	−0.0027 (6)	0.1064 (6)	0.4783 (6)	0.0051 (5)	0.0024 (4)	0.0040 (5)	0.0008 (8)	0.0004 (9)	0.0006 (8)
N(46)	0.1125 (5)	0.8863 (6)	0.4762 (6)	0.0025 (4)	0.0028 (4)	0.0055 (5)	0.0018 (7)	0.0030 (8)	0.0017 (9)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(11)	0.5904 (10)	0.6386 (11)	0.2101 (11)	5.5 (3)	C(31)	0.2923 (8)	0.3617 (9)	0.3808 (9)	4.0 (3)
C(12)	0.1608 (9)	0.2471 (9)	0.1289 (9)	4.3 (3)	C(32)	0.6761 (10)	0.0112 (10)	0.2995 (11)	5.2 (3)
C(13)	0.7912 (11)	0.8189 (12)	0.1599 (12)	6.5 (4)	C(33)	0.4366 (9)	0.1636 (10)	0.4468 (10)	4.6 (3)
C(14)	0.4238 (10)	0.0261 (10)	0.1425 (11)	5.3 (3)	C(34)	0.5862 (8)	0.4073 (9)	0.3573 (9)	4.2 (3)
C(15)	0.8063 (11)	0.4884 (12)	0.0688 (12)	6.4 (4)	C(35)	0.3175 (8)	0.6221 (9)	0.3511 (9)	4.1 (3)
C(16)	0.4525 (8)	0.2941 (8)	0.1077 (8)	3.4 (2)	C(36)	0.4697 (12)	0.8402 (12)	0.3377 (13)	6.8 (4)
C(21)	0.0601 (7)	0.8274 (8)	0.0372 (8)	3.3 (2)	C(41)	0.8031 (12)	0.6227 (13)	0.3935 (13)	7.3 (4)
C(22)	0.3115 (9)	0.4881 (11)	0.0449 (10)	5.0 (3)	C(42)	0.8873 (9)	0.8659 (9)	0.4250 (10)	4.5 (3)
C(23)	0.1042 (8)	0.6441 (9)	0.2114 (9)	3.7 (2)	C(43)	0.1688 (8)	0.0201 (9)	0.2765 (9)	4.0 (2)
C(24)	0.7419 (8)	0.2609 (9)	0.2067 (9)	3.9 (2)	C(44)	0.0159 (9)	0.4122 (10)	0.3087 (9)	4.6 (3)
C(25)	0.3850 (11)	0.7590 (12)	0.0838 (12)	6.3 (4)	C(45)	0.9281 (9)	0.1629 (10)	0.4120 (10)	5.0 (3)
C(26)	0.9565 (10)	0.0502 (11)	0.1252 (11)	5.1 (3)	C(46)	0.1927 (9)	0.8307 (10)	0.4471 (10)	4.5 (3)

[a] Figures in parentheses are the estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal paramater is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

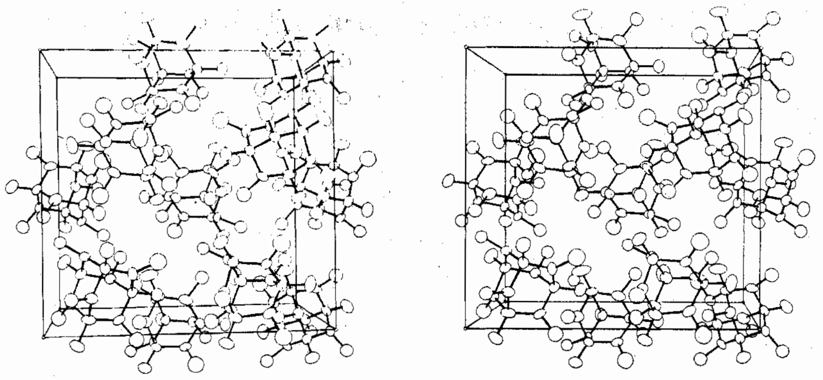

Figure 4. ORTEP stereoview of the unit cell of $O_4P_4(NMe)_6$ showing the molecular packing.

Table II. Refined Positional and Anisotropic Thermal Parameters[a,b] for $P_4S_4(NMe)_6$

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
				(A) Data Recorded at 3 °C					
S(1)	0.111 (1)	0.3131 (6)	0.1948 (9)	0.058 (2)	0.0101 (7)	0.034 (1)	−0.001 (3)	−0.045 (3)	−0.020 (2)
S(2)	0.122 (1)	0.2621 (17)	0.2396 (13)	0.025 (2)	0.0687 (20)	0.040 (1)	−0.020 (3)	0.004 (3)	−0.083 (2)
P(1)	0.0571 (4)	0.1426 (4)	0.1003 (4)	0.0156 (4)	0.0206 (5)	0.0165 (3)	−0.0022 (9)	−0.0072 (8)	−0.0184 (7)
N(1)	0.180 (1)	0.074 (1)	0.001 (1)	0.017 (1)	0.014 (1)	0.022 (1)	−0.009 (3)	0.004 (3)	−0.003 (3)
N(2)	0.000 (0)	0.000 (0)	0.184 (1)	0.025 (2)	0.035 (3)	0.006 (1)	0.027 (5)	0.000 (0)	0.000 (0)
C(1)	0.327 (2)	0.101 (2)	0.030 (2)	0.013 (2)	0.033 (3)	0.041 (3)	−0.013 (4)	0.001 (5)	−0.025 (6)
C(2)	0.000 (0)	0.000 (0)	0.336 (2)	0.060 (7)	0.045 (6)	0.012 (3)	0.028 (16)	0.000 (0)	0.000 (0)
				(B) Data Recorded at 22 °C					
S(1)	0.1104 (8)	0.3089 (7)	0.2054 (6)	0.030 (1)	0.0176 (7)	0.0245 (8)	−0.004 (2)	−0.012 (2)	−0.023 (1)
S(2)	0.1333 (24)	0.2143 (23)	0.2638 (20)	0.029 (3)	0.0344 (33)	0.0313 (22)	−0.007 (5)	−0.018 (5)	−0.032 (4)
S(3)	0.2056 (62)	0.3029 (51)	0.1359 (31)	0.032 (7)	0.0186 (53)	0.0027 (33)	−0.031 (9)	−0.005 (8)	−0.011 (7)
P(1)	0.0563 (4)	0.1430 (5)	0.1009 (4)	0.0152 (4)	0.0227 (5)	0.0180 (3)	−0.0012 (9)	−0.0083 (8)	−0.0206 (7)
N(1)	0.178 (1)	0.075 (1)	0.001 (1)	0.015 (1)	0.014 (1)	0.024 (2)	−0.009 (3)	0.003 (3)	0.001 (3)
N(2)	0.000 (0)	0.000 (0)	0.182 (1)	0.019 (2)	0.030 (3)	0.008 (1)	0.014 (5)	0.000 (0)	0.000 (0)
C(1)	0.335 (2)	0.100 (2)	0.026 (2)	0.016 (2)	0.028 (3)	0.038 (3)	−0.007 (5)	−0.008 (5)	−0.021 (6)
C(2)	0.000 (0)	0.000 (0)	0.336 (2)	0.044 (6)	0.034 (4)	0.012 (2)	0.020 (11)	0.000 (0)	0.000 (0)

[a] The figures in parentheses are the estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table III. Mean Values of Distances (Å) and Angles (deg) in $X_4P_4(NMe)_6$ (X = O, S) Averaged over All Crystallographically Independent Ones[a]

(A) $O_4P_4(NMe)_6$

P–N	1.67 (2)	∠N–P–N	104 (2)
P–O	1.45 (1)	∠N–P–O	114 (1)
P–P	2.88 (1)	∠P–N–P	119 (1)
N–C	1.52 (5)	∠P–N–C	116 (3)

(B) $S_4P_4(NMe)_6$

	this work		Hunter and Cordes[10]
	3 °C	22 °C	
P–N	1.656 (14)	1.652 (13)	1.66 (3)
P–S	1.912 (24)	1.937 (15)	1.93 (2)
P–P	2.89 (3)	2.90 (3)	not reported
N–C	1.47 (3)	1.52 (2)	1.45 (5)
∠N–P–N	103 (2)	103 (2)	103 (2)
∠N–P–S	115 (5)	116 (5)	116 (2)
∠P–N–P	120.6 (5)	121.7 (4)	124 (3)
∠P–N–C	119 (1)	119 (1)	118 (2)

[a] See ref 11 for definition of uncertainty intervals, Figure 5 for graphical presentation of the range of P–N distances, and supplementary tables for individual values.

range of values obtained for the 12 P–N distances, from 1.64 to 1.67 Å, is not surprising when viewed in that context. Nonetheless, we are again faced with a sizable uncertainty, 0.013 Å, in the average value, 1.652 Å. In the case of $O_4P_4(NMe)_6$, there are four molecules in the asymmetric unit[12] and thus the P–N distance is evaluated 48 times; unfortunately, there is again such a spread in the individual numbers that there is again a discouragingly large uncertainty, 0.020 Å, in the mean value, 1.667 Å.

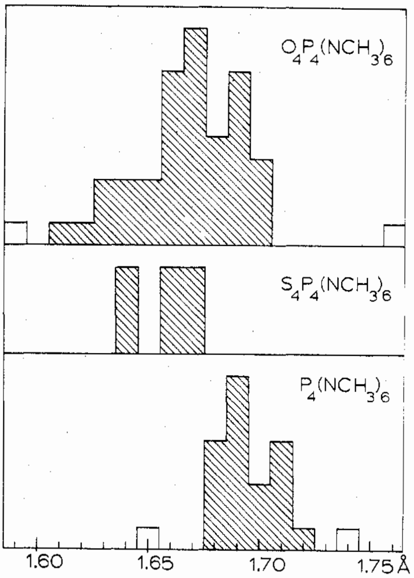

Figure 5. Histograms of the crystallographically independent P–N distances found in $P_4(NMe)_6$, $S_4P_4(NMe)_6$, and $O_4P_4(NMe)_6$. The extreme values in open boxes were omitted when computing averages and their uncertainty intervals.

It will be seen in later parts of this series that similar ranges and consequent uncertainties occur for all of the other structures we have examined in the course of this work. Clearly, there must be certain properties of all of the molecules in this class that give rise to this general lack of precision in atomic positions for their crystals. One of these is obviously the quasi-spherical nature of some of them, namely, $P_4(NMe)_6$ and the two whose structures are reported here. Sphere-like molecules and ions naturally have a tendency toward rotational disordering and/or large amplitudes of librational motion in crystals. In fact, for $P_4(NMe)_6$ this tendency is so great that there is a transition at 56 °C to a distinct plastic phase, characterized by virtually free rotation.[13]

In addition to the consequences of the sphericity of these molecules, other difficulties may arise from the fact that these molecules are hollow and likely to be somewhat flexible or deformable. Since they occupy positions of less than cubic symmetry in the crystals, they are acted upon by forces capable of distorting them from their intrinsic T_d symmetry. It is possible that for molecules such as these, displacements of individual atoms by distances of the order of several hundredths of an angstrom might result.

Finally, in connection with both of the above properties, it should be reported that crystals of all of the compounds that we shall report on in this series of papers have exhibited an unusually high sensitivity to macroscopic mechanical damage. Crystals that have been subjected to even slight external stresses become partly or wholly translucent, and translucent crystals have generally given broader diffraction lines than transparent ones.

The structural changes through the series $[P_4(NMe)_6]$, $S_4[P_4(NMe)_6]$, and $O_4[P_4(NMe)_6]$ may be compared to those in the analogous set of compounds $[P_4O_6]$,[14] $S_4[P_4O_6]$,[15] and $O_4[P_4O_6]$,[16] where in both cases we use square brackets to emphasize the existence of the central P_4X_6 core, of T_d symmetry, that maintains its integrity throughout the series. In both series it is clear that attachment of the four S or O atoms to the phosphorus atoms has only a slight effect upon the internal P–O or P–N bond lengths. The experimental uncertainties in the bond lengths are sufficiently large that while small decreases appear to result, the magnitudes of these are highly uncertain except in one case. Thus, in the first of the above series the P–N distances are 1.695 (12), 1.656 (14), and 1.67 (2) Å, while in the second they are 1.638 (3), 1.61 (2), and 1.604 (4) Å. A consistent decrease of about 0.03 Å from P_4X_6 to $Y_4P_4X_6$ is probable, but in no individual case can the statistical validity of the decrease be strongly argued.

Cruickshank showed,[17] some time ago, that for bonds of this general type (i.e., S–O, P–O, P–N, Si–O) with orders from 1 to 2, the derivative of bond order with respect to bond length (Å) is in the range of 2.5–3.0. Thus, changes of 0.03 Å correspond to increases in the π bonding of, at most, about 0.1 unit of bond order. While this is not very much, it is a significant fractional change, since, again according to Cruickshank's graph, for P–O bonds, the π-bond order in P_4O_6 is only about 0.2. Presumably a valid curve for P–N bonds can be obtained from that given for P–O bonds by moving it along the bond length axis by 0.04 Å, the difference in the single-bond covalent radii of the N and O atoms. On this basis, the π-bond order in $P_4(NMe)_6$ is about 0.15. It is also important to remember that even small changes in the individual P–N bond energies will be significant for one of these molecules as a whole because there are 12 such bonds.

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Registry No. $O_4P_4(NMe)_6$, 58979-11-6; $S_4P_4(NMe)_6$, 37747-07-2.

Supplementary Material Available: Tables of structure factors and complete tables of individual bond lengths and angles (32 pages). Ordering information is given on any current masthead page.

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(12) It is unusual to have so many molecules in the asymmetric unit but by no means unprecedented. Dr. Michael Brice of the Cambridge Crystallographic Data Centre at Cambride University has found, from a search of their files, that there are at least 34 other cases in which 4 identical molecules constitute the asymmetric unit and at least 17 cases in which there are more than 4.

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