Selective Redistribution Reactions of Tetraphosphorus Hexaoxide; Crystal Structure of P₄O₆NC₆H₅

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P_4O_6NR (R = $-Ph$, $-C_2H_4Ph$, $-n-C_6H_{13}$, $-SO_2Me$, $-CO_2Et$) are obtained from the reaction of tetraphosphorus hexaoxide with organic azides; the P_4O_5N cage-like structure is confirmed by ^{31}P NMR spectroscopy and X-ray structure analysis of $P_4O_6NC_6H_5$.

Tetraphosphorus hexaoxide is in principle available on a technical scale. As a starting material in organophosphorus chemistry, it seems to show several advantages over phosphorus trichloride, since the use of the latter produces large amounts of undesirable chlorine compounds, in particular hydrochloric acid requiring expensive recycling or waste management.[1] Therefore, controlled reactions of tetraphosphorus hexaoxide have always been of great interest in phosphorus chemistry.

While the reactions of P_4O_6 with reagents like P_4S_{10}, Ph_3PO or Se lead to the formation of oxidation products while preserving the cage-like P_4O_6 structure,[2] the reactions with reagents like alcohols, amines or aldehydes usually result in the complete fragmentation of the P_4O_6 cage.[3,4] Selective redistribution reactions involving the cage seem to be kinetically inhibited at low temperatures, and not controllable at higher temperatures.

In this paper, we discuss the selective reaction of organic azides with tetraphosphorus hexaoxide. Evolving molecular nitrogen, these reactions lead to the formation of a P_4O_5N cage as a definite derivative of P_4O_6, in good yields.† These are the first known examples of an oxygen–nitrogen redistribution reaction with preservation of a cage-like structure. So far, we have not been able to determine the mechanism of the reaction. The molecular structures of the products are determined by

^{31}P NMR spectroscopy (see Table 1), the molecular and crystal structure of $P_4O_6NC_6H_5$ is revealed by X-ray structure analysis (see Fig. 1).‡

As one would expect, the phosphorus–nitrogen bonds [P(1)–N and P(3)–N] are slightly longer than the corresponding phosphorus–oxygen bonds [P(1)–O(2)/O(5) and P(2)–O(2) or P(4)–O(5), respectively; see Fig. 1].

The known distortion of the P_4O_6 cage due to the addition of a terminally bonded oxygen atom[5,6] is also observed in the P_4O_5N cage. The P–O and P–N bonds starting from the pentavalent phosphorus atom [P(1)–O(2)/O(5) and P(1)–N] are significantly shorter than those starting from the trivalent phosphorus atoms [P(2)–O(2) or P(4)–O(5) and P(3)–N, respectively].

The configuration around the nitrogen atom is essentially planar [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°]. This is due to the interaction of π-acceptor orbitals of the more electropositive phosphorus atoms with the nonbonding orbital of nitrogen. If this interaction is larger than the competing σ-effect, the planar structure will be more stable than the pyramidal one.[7] 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°.

The trends in bond angles at the oxygen and nitrogen atoms [P–O–P 126°, P–N–P 120°] agree with those predicted using the VSEPR concept.
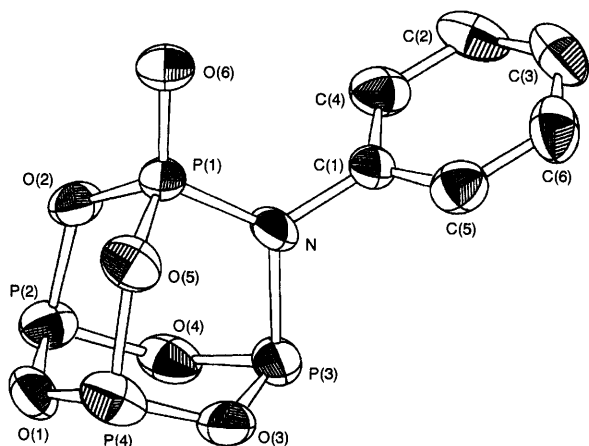
Fig. 1 Molecular structure of $P_4O_6NC_6H_5$; selected bond distances (Å) and angles (°): P(1)–O(2), 1.575(3), P(1)–O(5) 1.578(3), P(1)–N 1.643(4), P(1)–O(6) 1.444(3), P(2)–O(2) 1.679(3), P(4)–O(5) 1.665(3), P(3)–N 1.724(4), P(3)–O(3) 1.640(4), P(4)–O(3) 1.609(4), N–C(1) 1.447(5), P(1)–N–C(1) 122.9(3), 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)

Footnotes

Table 1 ^{31}P NMR shifts of P_4O_6–N derivatives (300 MHz, toluene, H_3PO_4 ext.)

Compound	δ [P(2)/P(4)][a]	δ [P(3)][a]	δ [P(1)][a]
$P_4O_6NC_6H_5$	140.2 (d, –P(3); 50.8 Hz)	136.9 [t, –P(2)/P(4); 50.8 Hz]	−43.1
$P_4O_6NC_2H_4(C_6H_5)$	142.7 (d, –P(3); 48.3 Hz)	145.7 [t, –P(2)/P(4); 48.3 Hz]	−39.3
$P_4O_6NC_6H_{13}$	143.3 (d, –P(3); 47.5 Hz)	148.0 [t, –P(2)/P(4); 47.5 Hz]	−39.5
$P_4O_6NSO_2CH_3$	132.0 (d, –P(3); 55.7 Hz)	117.4 [t, –P(2)/P(4); 55.7 Hz]	−47.0
$P_4O_6NCO_2C_2H_5$	132.6 (d, –P(3); 54.5 Hz)	124.7 [t, –P(2)/P(4); 54.5 Hz]	−48.1

[a] See Fig. 1

fractometer using graphite-monochromated Mo-Kα radiation [λ = 0.71073 Å, μ = 0.7 mm^{-1}] with ω-θ scans. Structure solution by direct methods, refinement by full matrix-least-squares analysis on F^2. wR^2 = 0.114, R = 0.042 for 1408 $F_o > 4\sigma(F_o)$.[13]

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors Issue No. 1.

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