Synthesis and *X*-Ray Crystallographic Characterization of a Stable Dioxadiphosphetane

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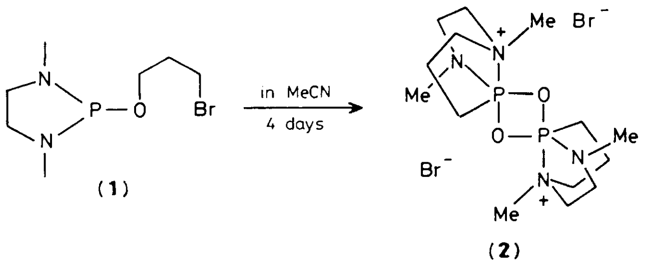
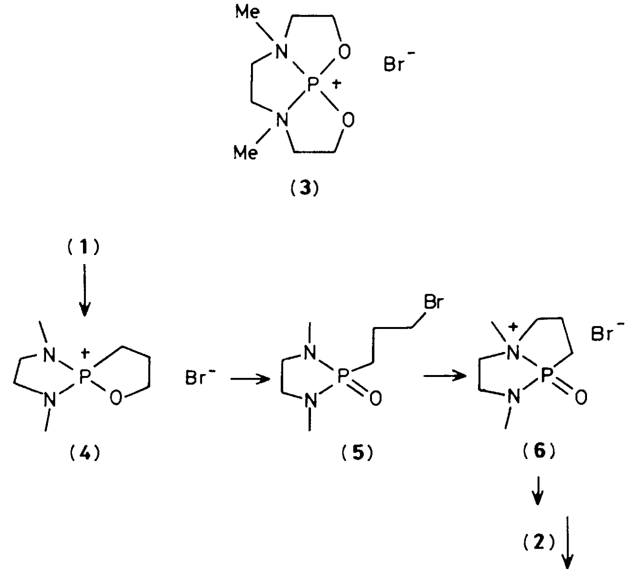
In acetonitrile 2-(3-bromopropoxy)-1,3-dimethyl-1,3,2-diazaphospholidine (**1**) rearranges to give a structurally stable dioxadiphosphetane (**2**), which has been characterized by *X*-ray crystallography

The marked stability of the P=O bond is a ubiquitous feature of the chemistry of phosphorus(v). To date no dioxadiphosphetane (which may be considered to be derived from the cyclic dimerization of two P=O bonds) has been structurally characterized, although the formation of dioxadiphosphetane intermediates has been postulated recently to account for ^{18}O scrambling data for the reaction of phosphoryl esters with phosphoryl chlorides[1] and for the oxidation of ADPαS to ADP with BrCN in $H_2{}^{18}O$.[2] In this communication we report the isolation and structural characterization of a stable dioxadiphosphetane.

When a solution of 2-(3-bromopropoxy)-1,3-dimethyl-1,3,2-diazaphospholidine[3] (**1**) in acetonitrile is kept at room temperature for 4 days, the dioxadiphosphetane dication (**2**) is obtained as a white crystalline, rather insoluble product (*ca.* 40% overall yield). The unusual dimeric nature of (**2**) has been shown by single crystal *X*-ray diffraction (Figure 1).† Both *cisoid* and *transoid* forms are observed in the disordered centrosymmetric dication. The co-ordination geometries at phosphorus are essentially trigonal bipyramidal, with one axial and one equatorial bridging P–O bond at each P. The small O(1) PO(1′) bond angle [82.6(2)°] and slightly enlarged angles N(2)P(1)O(1) and C(5)P(1)O(1) are the only significant distortions away from normal bond angles. The axial P–N(quaternary) bond length [1.934(6) Å] is notably long, though comparable to the P–N distance of 1.986 Å observed in





Scheme 1

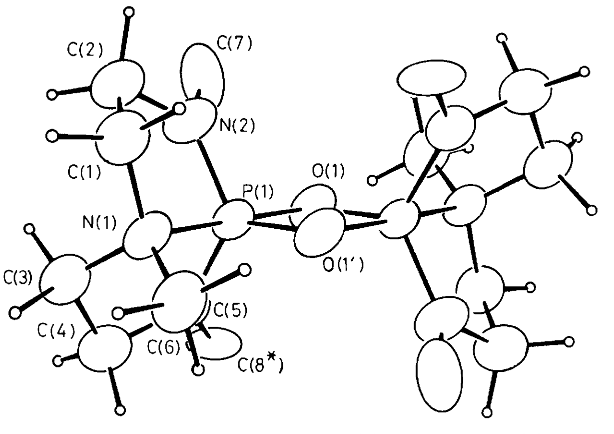


Figure 1. The molecular structure of (**2**) as determined by single crystal *X*-ray diffraction. Selected bond lengths (Å): P(1)–O(1) 1.735(5), P(1)–O(1′), 1.593(5), P(1)–N(1) 1.934(6), P(1)–N(2) 1.655(8), P(1)–C(5) 1.696(7). Bond angles (°): O(1)P(1)O(1′) 82.6(2), O(1)P(1)N(1) 173.3(2), O(1)P(1)N(2) 95.0(3), O(1)P(1)C(5) 94.3(3), O(1′)P(1)N(1) 90.7(2), O(1′)P(1)N(2) 118.9(3), O(1′)P(1)C(5) 120.9(3). *N.B.* C(8*) is a consequence of the *cisoid/transoid* disorder of N(2)C(7) and C(5).

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† *Crystal data:* $C_7H_{16}BrN_2OP$, monoclinic, space group $P2_1/n$, a = 10.306(2), b = 13.899(2), c = 7.572(2) Å, β = 105.65(2)°, V = 1044.4 Å^3, D_c = 1.62 g cm^{-3} for Z = 4 (two dimers), Mo-K_α radiation (λ = 0.7169 Å), μ (Mo-K_α) = 40.1 cm^{-1}. Unit cell dimensions by least-squares refinement of 25 reflections ($11.0 < \theta < 15.9°$). Data collection using ω–2θ scans over scan ranges (ω) of $(0.95 + 0.35\tan\theta)°$ (profiles somewhat broad). Scan speeds selected to give $I/\sigma(I) \geqslant 25$ within max. scan time of 75 s. No significant variations in intensities of 3 standards collected every 9000 s of exposure. 2727 Reflections in quadrant h, k, $\pm l$ with $2\theta \leqslant 55°$ collected. Lorentz and polarization corrections applied to all data. Exclusion of systematically absent or zero F_o gave 2149 data.

Structure solution: Patterson for Br and P, other atoms by F_o or ΔF Fourier maps. Structure found to have disordered *cisoid/transoid* forms of the dimer in lattice (see text). To avoid correlation problems, sum of population parameters (PPs) for disordered Me group fixed at 1.0. Approximately 60:40 ratio used to scale PPs of N(2) and C(5), which were then fixed in final refinements. A ΔF Fourier analysis at this point gave some indications for the H atoms at the disordered $C(7/8)H_3$ positions and these were included with optimized geometries and the same PPs as the C(7/8) atoms. Least-squares refinement minimizing $\Sigma w\Delta F^2$ converged (max. $\Delta/\sigma = 0.24$) to final residuals R_1 = 0.0463 (R_w = 0.0476) for 1031 reflections with $I > 3\sigma(I)$. Weights given by $w = [\sigma^2(F) + 0.001017\ F^2]^{-1}$ and a final ΔF Fourier map contained a few small peaks ($\leqslant$0.75 e Å^{-3}) within 1 Å of the Br ion. Programs: SDP package and SHELX on PDP 11/23 and Gould 9705 computers, respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

the phosphatrane $[HP(OCH_2CH_2)_3N]^+BF_4^-$.[4] (Typical PN bond lengths are *ca.* 1.65 Å; sum of covalent radii is 1.8 Å.) The P–O distances of 1.593(5) and 1.735(5) Å are consistent with their equatorial and axial dispositions.[5] The only other comparable Group V structure is that of triphenylstibine oxide, which has recently been shown to be dimeric with an Sb_2O_2 bridge structure.[6]

The formation of (**2**) from (**1**) contrasts with the known behaviour of 2-(2-bromoethoxy)-1,3-dimethyl-1,3,2-diazaphospholidine, which in acetonitrile disproportionates to give 2-bromo-1,3-dimethyl-1,3,2-diazaphospholidine and the catonic species (**3**).[7] A suggested mechanism for the formation of (**2**) is outlined in Scheme 1. When a solution of (**1**) in $CDCl_3/CD_3CN$ (1 : 2 v/v) is kept at +3 °C for 7 days the major solution species formed has ^1H and ^{31}P n.m.r. characteristics consistent with structure (**5**) [*e.g.* δ_P +39.0 p.p.m., *cf.* δ_P for $(Me_2N)_2P(=O)CH_3$ +38.0 p.p.m. (ref. 8)]. After a further period at room temperature crystals of (**2**) are obtained.

The isolation of the unusual dimeric dioxadiphosphetane (**2**) instead of the monomeric P=O bonded structure (**6**) is probably a consequence of (i) ring strain effects favouring trigonal bipyramidal (*vs.* tetrahedral) co-ordination at P; and (ii) the insolubility of (**2**) in acetonitrile.

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References

1 P. M. Cullis, P. B. Kay, and S. Trippett, *J. Chem. Soc., Chem. Commun.*, 1985, 1329.
2 R. Iyengar, H.-T. Ho, R. D. Sammons, and P. A. Frey, *J. Am. Chem. Soc.*, 1984, **106**, 6038.
3 F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *J. Am. Chem. Soc.*, 1967, **89**, 6276.
4 J. C. Clardy, D. S. Milbrath, J. P. Springer, and J. G. Verkade, *J. Am. Chem. Soc.*, 1976, **98**, 623.
5 R. Sarma, F. Ramirez, B. McKeever, J. F. Marecek, and S. Lee, *J. Am. Chem. Soc.*, 1976, **98**, 581.
6 J. Bordner, G. O. Doak, and T. S. Everett, *J. Am. Chem. Soc.*, 1986, **108**, 4206.
7 J. Sliwa and J. P. Picavet, *Tetrahedron Lett.*, 1977, 1583.
8 R. A. Y. Jones and A. R. Katritzky, *Angew. Chem.*, 1962, **74**, 60.

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