

Acta Crystallographica Section C

Crystal Structure
Communications

ISSN 0108-2701

4,4,6,6-Tetrachloro-2,2-(2,2-dimethylpropane-1,3-diyl-dioxy)-1,3,5,2 λ^5 ,4 λ^5 ,6 λ^5 -triazatriphosphorine

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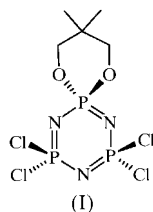
Received 31 August 2001

Accepted 18 September 2001

The title spirocyclic compound (alternative name: 2,2,4,4-tetrachloro-9,9-dimethyl-7,11-dioxo-1,3,5-triaza-2 λ^5 ,4 λ^5 ,6 λ^5 -triphosphaspiro[5.5]undeca-1,3,5-triene), C₅H₁₀Cl₄N₃O₂P₃, does not contain alternating long-short P–N bond lengths in the phosphazene ring [P–N 1.559 (2)–1.596 (2) Å], as are observed in other analogous spirocyclic compounds. The six-membered phosphazene ring has a chair conformation in the solid state, but a conformational equilibrium in solution is indicated by NMR spectroscopy.

Comment

We are interested in utilizing substituted cyclotriphosphazenes as bases in our synthetic research. Since the most readily accessible among these, N₃P₃Cl₆, (I), has six reactive Cl atoms that can affect its utility, we wished to reduce the number of functionalities. One of the easiest ways to do this is to treat (I) with a suitable difunctional reagent and obtain 'spiro' or 'ansa' type products (Contractor *et al.*, 1984; Kumaraswamy *et al.*, 1999; Chandrasekhar & Thomas, 1993). Since tetracoordinate P^V compounds with six-membered rings at the P atom are more stable to hydrolysis than those with five-membered rings, the diol 2,2-dimethyl-1,3-propanediol, which is cheaper than 1,3-propanediol, was used as the starting material. Differences



in the reactivity patterns of these two diols were also studied, as observed in the reaction of the cyclodiphosphazane [CIPN-'Bu]₂, (III) (Kumaravel *et al.*, 1987; Kommana & Kumara Swamy, 2000). We found that the reaction of (I) with 2,2-dimethyl-1,3-propanediol gave the title spirocyclic compound, (II), as the only product. We report herein the X-ray structure of (II).

An ORTEX (McArdle, 1995) drawing of (II) is shown in Fig. 1. The bond distances and angles are in the normal ranges expected for compounds of this type (Chandrasekhar & Thomas, 1993). The P1–N1 distance is the longest, but P1–N3 is close in length to N2–P3 and N2–P2. This pattern is slightly different from the patterns observed in analogous monospirocyclic cyclotriphosphazenes (Contractor *et al.*, 1985; Kumaraswamy *et al.*, 1999), wherein a long-short-long pattern for the ring P–N bond lengths was noted. The P–Cl bond lengths are within the normal range observed for analogous compounds (Contractor *et al.*, 1984; Kumaraswamy *et al.*, 1999).

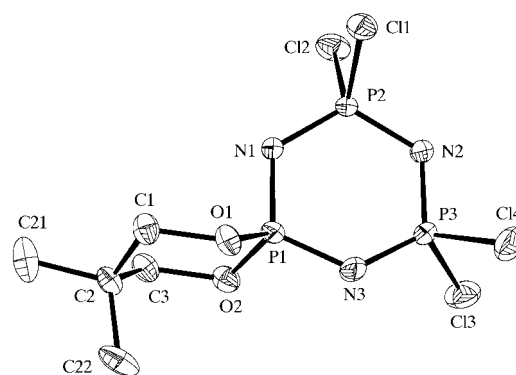


Figure 1

The molecular structure of (II) showing the atom numbering scheme. Displacement ellipsoids are shown at the 25% probability level and H atoms have been omitted for clarity.

The phosphazene ring can be considered to be planar, the maximum deviation from planarity of 0.135 Å being observed for N3. The 1,3,2-dioxaphosphorinane ring has the usual chair form, with atom C2 above and P1 below the mean plane containing atoms O1, O3, C1 and C3. Since this feature would make the two methyl groups and the two H atoms of each OCH₂ group inequivalent [for examples giving NMR in solution and solid-state X-ray structures, see Muthiah *et al.* (2000)], the observed ¹H NMR spectrum in solution (*i.e.* equivalence of the methyl and OCH₂ H atoms) suggests a conformational equilibrium in solution.

Regarding intermolecular contacts, we note that atom C3 is close to O3 of a related molecule [C3...O3ⁱ 3.352 (3) Å; symmetry code: (i) 2 – x, –y, 1 – z] and *vice versa*. The corresponding H3B...O3 distance is 2.88 Å. Although this is a minor point, it could be important in connection with our understanding of the crystal packing and it has not been considered in the cyclophosphazene structures reported to date.

Experimental

A solution of 2,2-dimethyl-1,3-propanediol (1.04 g, 10 mmol) and triethylamine (2.02 g, 20 mmol) in toluene (10 ml) was added dropwise over a period of 10 min with continuous stirring to a solution of N₃P₃Cl₆ (3.48 g, 10 mmol) in toluene (10 ml). The reaction mixture

organic compounds

was then heated under reflux for 8 h, followed by filtration and removal of the solvent. The solid obtained (m.p. 427–428 K) was crystallized from dichloromethane–hexane (1:4); yield 3.23 g, 85%. Crystals were used for X-ray examination as obtained. ^1H NMR (CDCl_3 , δ , p.p.m.): 1.10 [s, 6H, $\text{C}(\text{CH}_3)_2$], 4.12 (d, $^3J_{\text{P-H}} = 14.0$ Hz, 4H, OCH_2); ^{31}P NMR (p.p.m.): 1.3 (t, $^2J_{\text{PP}} = 69.6$ Hz, P_{spiro}), 22.6 (d, $^2J_{\text{PP}} = 69.6$ Hz, PCl_2).

Crystal data

$\text{C}_5\text{H}_{10}\text{Cl}_4\text{N}_3\text{O}_2\text{P}_3$	$D_x = 1.714$ Mg m $^{-3}$
$M_r = 378.87$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 12.106$ (2) Å	$\theta = 9.5$ – 12.0°
$b = 7.708$ (2) Å	$\mu = 1.13$ mm $^{-1}$
$c = 15.776$ (2) Å	$T = 293$ (2) K
$\beta = 93.997$ (10) $^\circ$	Rectangular block, colourless
$V = 1468.5$ (5) Å 3	$0.4 \times 0.3 \times 0.2$ mm
$Z = 4$	

Data collection

Enraf–Nonius MACH3 diffractometer	$R_{\text{int}} = 0.014$
Profile data from ω scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: ψ scan (DATCOR; Reibenspies, 1989)	$h = 0 \rightarrow 14$
$T_{\text{min}} = 0.662$, $T_{\text{max}} = 0.806$	$k = 0 \rightarrow 9$
2693 measured reflections	$l = -18 \rightarrow 18$
2571 independent reflections	3 standard reflections
2135 reflections with $I > 2\sigma(I)$	frequency: 90 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0460P)^2 + 0.6318P]$
$R(F) = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.083$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.29$ e Å $^{-3}$
2571 reflections	$\Delta\rho_{\text{min}} = -0.28$ e Å $^{-3}$
157 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.0198 (11)

All H atoms were placed geometrically and refined using a riding model with SHELXL97 (Sheldrick, 1997) defaults.

Data collection: CAD-4 Software (Enraf–Nonius, 1989); cell refinement: CAD-4 Software; data reduction: SDP-Plus (Frenz, 1985); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEX (McArdle, 1995); software used to prepare material for publication: SHELXL97.

Funding for this work was provided by the Council of Scientific and Industrial Research, New Delhi. We thank the

Table 1

Selected geometric parameters (Å, $^\circ$).

P1–N1	1.596 (2)	P2–N1	1.559 (2)
P1–N3	1.581 (2)	P2–N2	1.581 (2)
P1–O1	1.5656 (18)	P3–Cl3	1.9946 (10)
P1–O2	1.5613 (18)	P3–Cl4	1.9892 (11)
P2–Cl1	2.0034 (9)	P3–N2	1.582 (2)
P2–Cl2	1.9880 (9)	P3–N3	1.565 (2)
N1–P1–N3	116.26 (11)	Cl3–P3–Cl4	101.40 (5)
O1–P1–O2	104.57 (9)	N2–P3–Cl3	107.99 (10)
O1–P1–N1	109.52 (11)	N2–P3–Cl4	108.88 (10)
O1–P1–N3	107.88 (12)	N3–P3–Cl3	109.81 (10)
O2–P1–N1	109.22 (11)	N3–P3–Cl4	108.14 (10)
O2–P1–N3	108.75 (12)	N2–P3–N3	119.16 (11)
Cl1–P2–Cl2	100.29 (4)	P1–N1–P2	121.92 (13)
N1–P2–Cl1	110.11 (9)	P1–N3–P3	121.27 (13)
N1–P2–Cl2	109.45 (9)	P2–N2–P3	119.42 (13)
N1–P2–N2	118.54 (11)	Cl1–O1–P1	116.97 (15)
N2–P2–Cl1	108.95 (9)	C3–O2–P1	117.42 (15)
N2–P2–Cl2	107.93 (9)		

Department of Science and Technology (New Delhi) for setting up a single-crystal diffractometer at the University of Hyderabad.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1084). Services for accessing these data are described at the back of the journal.

References

- Chandrasekhar, V. & Thomas, K. R. J. (1993). *Struct. Bonding (Berlin)*, **81**, 41–113.
- Contractor, S. R., Hursthouse, M. B., Parkes, H. G., Shaw, L. S., Shaw, R. A. & Yilmaz, H. (1984). *J. Chem. Soc. Chem. Commun.* pp. 675–676.
- Contractor, S. R., Hursthouse, M. B., Shaw, L. S., Shaw, R. A. & Yilmaz, H. (1985). *Acta Cryst.* **B41**, 122–131.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Frenz, B. A. (1985). *SDP-Plus Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.
- Kommana, P. & Kumara Swamy, K. C. (2000). *Inorg. Chem.* **39**, 4384–4385.
- Kumaraswamy, S., Vijjulatha, M., Muthiah, C., Kumara Swamy, K. C. & Engelhardt, U. (1999). *J. Chem. Soc. Dalton Trans.* pp. 891–899.
- Kumaravel, S. S., Krishnamurthy, S. S., Cameron, T. S. & Linden, A. (1987). *Inorg. Chem.* **26**, 684–689.
- McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
- Muthiah, C., Praveen Kumar, K., Aruna Mani, C. & Kumara Swamy, K. C. (2000). *J. Org. Chem.* **65**, 3733–3737.
- Reibenspies, J. (1989). *DATCOR*. Texas A&M University, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.