# organic compounds

# 4′,4′,6′,6′-Tetrachloro-3,4-dihydro-3-(6-methylpyridin-2-yl)spiro-[1,3,2-benzoxazaphosphinine-2,2′-(2λ⁵,4λ⁵,6λ⁵-cyclotriphosphazene)]

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The title compound, $C_{13}H_{12}Cl_4N_5OP_3$, is a phosphazene derivative with a bulky substituted spirocyclic ring. The $C_3NPO$ spirocyclic ring has a twist-boat conformation, while the phosphazene ring has a very flattened boat conformation.

## Comment

The structures of derivatives of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with different substituents have been the subject of much interest in our laboratory, and our group has investigated some of the bulky substituted phosphazene derivatives (Tercan, Hökelek, Bilge, Özgüç & Kılıç, 2004; Tercan, Hökelek, Bilge, Natsagdorj *et al.*, 2004; Kılıç *et al.*, 1996). $N_3P_3Cl_6$, the standard compound for trimeric phosphazene derivatives, has been used in the preparation of novel small organocyclophosphazenes and polyorganophosphazenes (Allcock *et al.*, 1992; Olshavsky & Allcock, 1995). The structures of organic, inorganic or organometallic substituents are highly effective in determining the specific physical and chemical properties of phosphazene and polyphosphazene derivatives (Allcock *et al.*, 1996; Dembek *et al.*, 1991).

The reactions of $N_3P_3Cl_6$ with multidentate ligands afford spiro, ansa, bino and spiro-ansa phosphazene architectures (Dez *et al.*, 1999; Mathew *et al.*, 2000; Tercan, Hökelek, Bilge, Natsagdorj *et al.*, 2004). Recently, the stereogenic properties of dispirophosphazenes have been investigated crystallographically and *via* ³¹P NMR spectroscopy (Coles *et al.*, 2004). The crystal structures of $N_3P_3Cl_6$ (Bullen, 1971) and a few of its derivatives with bulky N/O groups have been reported (Tercan, Hökelek, Işıklan *et al.*, 2004). To the best of our knowledge, until now, the reactions of $N_3P_3Cl_6$ with *N*-[(2-hydroxyphenylmethyl)amino]-6-methylpyridine have only been investigated by our group. In contrast to our expectations, the resulting reaction led to the formation of only a

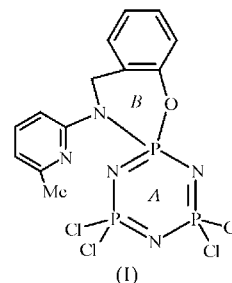novel spirophosphazene derivative, namely the title compound, (I), instead of ansa or bino phosphazene architectures.



(I)

Fig. 1 shows the molecular structure of (I), with the atomic numbering scheme. The phosphazene ring (*A*) is not completely planar, having a total puckering amplitude, $Q_T$, of 0.078 (2) Å (Cremer & Pople, 1975) and a flattened boat form [Fig. 2(*a*); $\varphi$ = 64.3 (16)° and $\theta$ = 96.1 (16)°]. Ring *A* has local mirror symmetry, with an axis passing through atoms N1 and P3, as can be deduced from the torsion angles (Table 1). The six-membered P3/N4/C7/C8/C13/O1 ring (*B*) has a total puckering amplitude of 0.480 (2) Å (Cremer & Pople, 1975) and a twist-boat form [Fig. 2(*b*); $\varphi$ = 138.6 (4)° and $\theta$ = 104.4 (14)°]. The sum of the bond angles around atom N4 [359.6 (2)°] shows that the configuration of this ring is planar.

In ring *A*, the P—N bond lengths are in the range 1.558 (3)–1.584 (3) Å and have a regular dependence on the distance from atom P3 in the ring, such that P3—N3 ≃ P3—N2 > P1—N1 ≃ P2—N1 > P2—N2 ≃ P1—N3. The P—N bonds of the phosphazene ring (Table 1) have double-bond character. However, the exocyclic P3—N4 bond [1.642 (3) Å] is at the lower limit for a single bond. In phosphazene compounds, P—N single and double bonds are generally in the ranges 1.628–1.691 and 1.571–1.604 Å, respectively (Allen *et al.*, 1987). The shortness of the P3—N4 bond in (I) indicates that electron release has occurred from the lone pairs of electrons of atom N4 to the phosphazene ring.
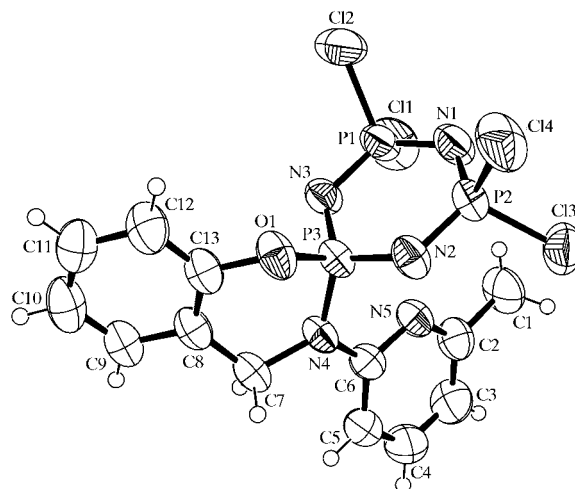


**Figure 1**
An *ORTEP*-3 (Farrugia, 1997) drawing of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
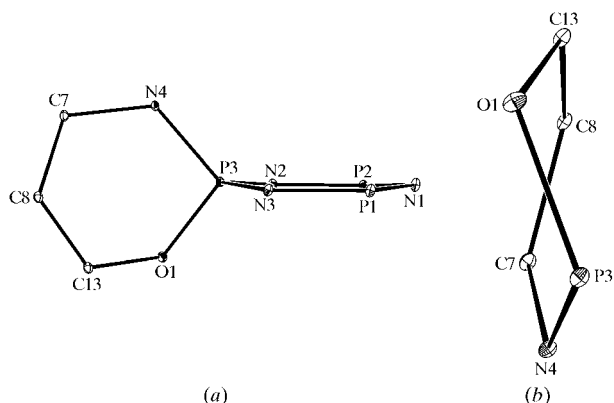
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**Figure 2**
The conformations of (*a*) the spirocyclic system and (*b*) the six-membered N/O ring in (I). The substituents have been omitted for clarity.
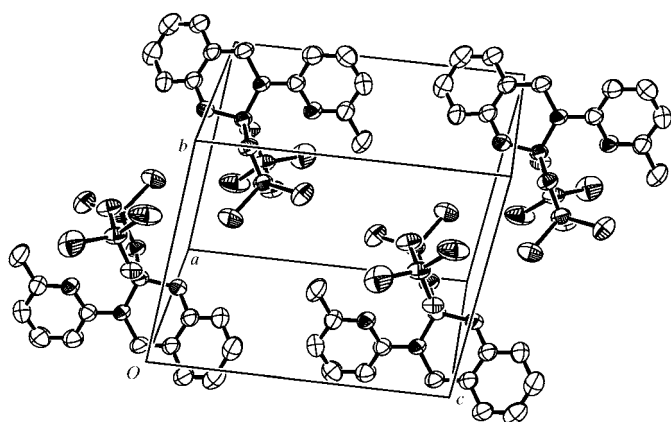


**Figure 3**
A packing diagram of (I).

In the phosphazene ring, the endocyclic N2—P3—N3 angle [116.45 (14)°] is smaller than and the exocyclic O1—P3—N4 angle [101.66 (13)°] is almost the same as those of the 'standard' compound $N_3P_3Cl_6$ (Bullen, 1971); these values are consistent with electron donation and withdrawal by the substituents in (I). In $N_3P_3Cl_6$, the corresponding angles are 118.3 (2)–118.5 (3) and 101.2 (1)–101.6 (1)°, respectively. The P2—N2—P3 and P3—N3—P1 bond angles in (I) are in the range 122.13 (18)–122.24 (17)°, while the P1—N1—P2 angle [119.66 (19)°] is decreased as a result of electron donation and withdrawal by the $N_3P_3$ ring (Kılıç *et al.*, 1996). These values are comparable to the mean value reported for $N_3P_3Cl_6$, *viz*. 121.4 (3)°.

As can be seen from the packing diagram (Fig. 3), the molecules are elongated parallel to the *c* axis and stacked along the *a* axis. Dipole–dipole and van der Waals interactions are also effective in the molecular packing.

## Experimental

For the preparation of the title compound, *N*-[(2-hydroxyphenylmethyl)amino]-6-methylpyridine (2.45 g, 11.4 mmol) in dry benzene (50 ml) was added slowly to a solution of $N_3P_3Cl_6$ (3.98 g, 11.4 mmol) and triethylamine (4.78 ml, 34.5 mmol) with stirring and refluxing at 253 K. After 30 min, the mixture was allowed to reach ambient temperature. The mixture was refluxed for 30 h, and then the preci-

pitated salts were filtered off and the solution evaporated under reduced pressure. The oily residue was crystallized from tetrahydrofuran/light petroleum (1:1) (m.p. 475 K; yield 5.58 g, 60%).

*Crystal data*

| | |
|---|---|
| $C_{13}H_{12}Cl_4N_5OP_3$ | $Z = 2$ |
| $M_r = 488.99$ | $D_x = 1.617$ Mg m$^{-3}$ |
| Triclinic, $P\bar{1}$ | Cu $K\alpha$ radiation |
| $a = 8.9834$ (1) Å | Cell parameters from 25 |
| $b = 9.5110$ (2) Å | reflections |
| $c = 11.9857$ (2) Å | $\theta = 11$–23° |
| $\alpha = 82.131$ (2)° | $\mu = 7.76$ mm$^{-1}$ |
| $\beta = 87.598$ (1)° | $T = 293$ (2) K |
| $\gamma = 81.992$ (2)° | Prism, colourless |
| $V = 1004.26$ (3) Å$^3$ | $0.40 \times 0.25 \times 0.20$ mm |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | $R_{int} = 0.031$ |
| | $\theta_{max} = 74.2°$ |
| Non-profiled $\omega$ scans | $h = -11 \rightarrow 11$ |
| Absorption correction: $\psi$ scan (North *et al.*, 1968) | $k = -11 \rightarrow 0$ |
| | $l = -14 \rightarrow 14$ |
| $T_{min} = 0.146$, $T_{max} = 0.212$ | 3 standard reflections |
| 4003 measured reflections | frequency: 120 min |
| 3909 independent reflections | intensity decay: 1% |
| 2661 reflections with $I > 2\sigma(I)$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.1278P)^2]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.063$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.166$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $S = 1.02$ | $\Delta\rho_{max} = 0.44$ e Å$^{-3}$ |
| 3274 reflections | $\Delta\rho_{min} = -0.37$ e Å$^{-3}$ |
| 236 parameters | Extinction correction: *SHELXL*97 |
| H-atom parameters constrained | Extinction coefficient: 0.088 (6) |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| O1—C13 | 1.406 (4) | P2—N1 | 1.573 (3) |
| O1—P3 | 1.576 (2) | P1—N3 | 1.558 (3) |
| P3—N2 | 1.582 (3) | P1—N1 | 1.576 (3) |
| P3—N3 | 1.584 (3) | N4—C6 | 1.408 (4) |
| P3—N4 | 1.642 (3) | N4—C7 | 1.494 (4) |
| P2—N2 | 1.565 (3) | | |
| | | | |
| C13—O1—P3 | 120.0 (2) | N3—P1—N1 | 119.54 (15) |
| O1—P3—N2 | 103.82 (14) | C6—N4—C7 | 116.4 (3) |
| O1—P3—N3 | 108.64 (16) | C6—N4—P3 | 120.3 (2) |
| N2—P3—N3 | 116.45 (14) | C7—N4—P3 | 122.9 (2) |
| O1—P3—N4 | 101.66 (13) | P1—N3—P3 | 122.24 (17) |
| N2—P3—N3 | 112.85 (15) | P2—N1—P1 | 119.66 (19) |
| N3—P3—N4 | 111.88 (14) | P2—N2—P3 | 122.13 (18) |
| N2—P2—N1 | 119.49 (16) | | |
| | | | |
| N1—P1—N3—P3 | −1.4 (3) | N3—P1—N1—P2 | −4.5 (3) |
| N2—P3—N3—P1 | 6.5 (3) | N1—P2—N2—P3 | 0.4 (3) |
| N2—P2—N1—P1 | 5.0 (4) | N3—P3—N2—P2 | −6.0 (3) |

H atoms were positioned geometrically at distances of 0.93 (CH), 0.96 (CH$_2$) and 0.97 Å (CH$_3$) from the parent C atoms; a riding model was used during the refinement process. The $U_{iso}$(H) values were constrained to be 1.2 (1.5 for methyl) times $U_{eq}$ of the carrier atom.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1184). Services for accessing these data are described at the back of the journal.

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