Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4′,4′,6′,6′-Tetrachloro-3-(4,6-dimethylpyridin-2-yl)-3,4-dihydrospiro[1,3,2-benzoxazaphosphinine-2,2′-(2λ^5,4λ^5,6λ^5-cyclotriphosphazene)]

Nagihan Çaylak,[a] Tuncer Hökelek,[a]* Orhan Büyükgüngör,[b] Hakan Dal,[c] Yasemin Süzen[c] and Zeynel Kılıç[d]

[a]Department of Physics, Hacettepe University, 06800 Beytepe, Ankara, Turkey, [b]Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, TR-55139, Kurupelit-Samsun, Turkey, [c]Department of Chemistry, Anadolu University, 26470 Yenibağlar, Eskişehir, Turkey, and [d]Department of Chemistry, Ankara University, 06100 Tandoğan, Ankara, Turkey

Correspondence e-mail: merzifon@hacettepe.edu.tr

Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.030
wR factor = 0.074
Data-to-parameter ratio = 15.0

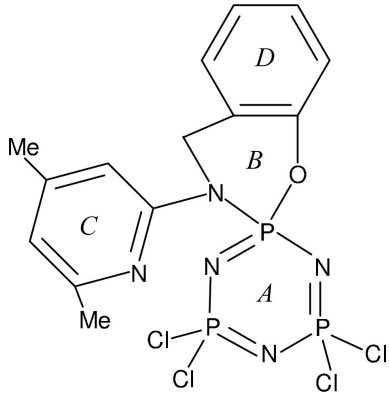
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 15 April 2005
Accepted 27 April 2005
Online 7 May 2005

The title compound, $C_{14}H_{14}Cl_4N_5OP_3$, is a phosphazene derivative with a bulky substituent attached through a spiro junction. The C_3NPO ring at the spiro junction has a twist–boat conformation, while the phosphazene ring has a flattened-boat conformation. The P_{spiro} atom is likely to be stereogenic.

Comment

In recent years, phosphazene derivatives have attracted considerable interest for a variety of reasons. They produce inorganic polymers with different organic and inorganic side groups (Uslu *et al.*, 2005). The stereogenic properties of phosphazenes have also been of great interest (Beşli *et al.*, 2003; Coles *et al.*, 2002), as has their use in the design of highly selective anticancer (Baek *et al.*, 2000), antibacterial (Konar *et al.*, 2000) and anti-HIV (Brandt *et al.*, 2001) agents. In addition, they have found practical application in the production of inflammable textile fibres, advanced elastomers (Blonsky *et al.*, 1986), rechargeable lithium batteries (Allcock, Napierala *et al.*, 1996) and biomedical materials (Allcock & Kwon, 1986).



(I)

Trimeric phosphazene, also known as hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, is considered to be the 'standard' compound in the field of phosphazene chemistry. It has been used in the preparation of novel small organocyclophosphazenes and phosphazene polymers with different substituents (Allcock *et al.*, 1992; Olshavsky & Allcock, 1995). In determining the specific physical and chemical properties of phosphazene and polyorganophosphazenes, the structures of organic, inorganic or organometallic substituents have been very effective (Allcock, Al-Shali *et al.*, 1996; Dembek *et al.*, 1991).

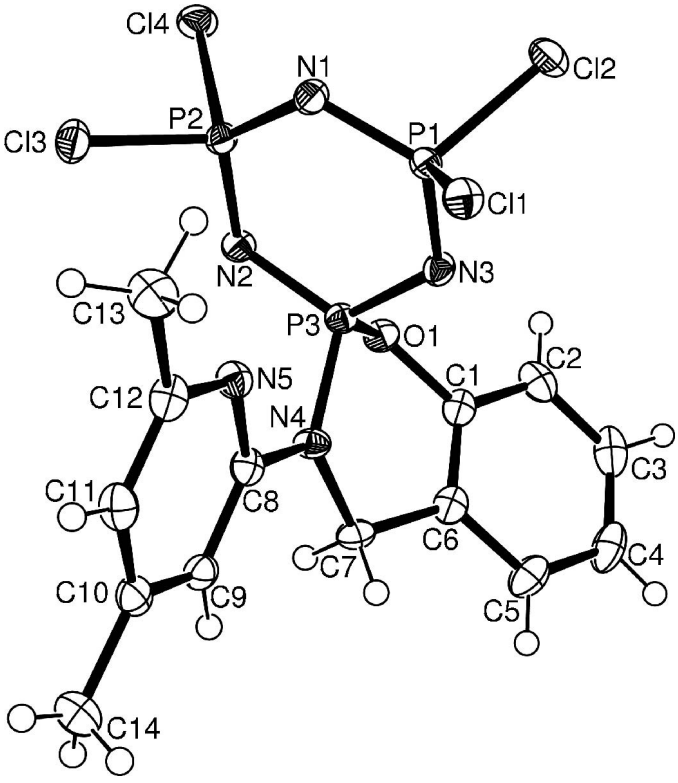


Figure 1
A drawing of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

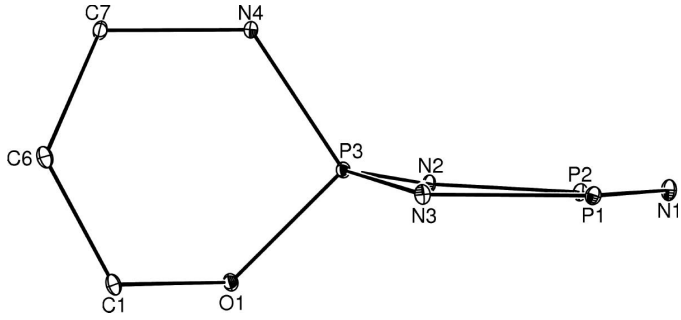


Figure 2
The orientations of the spiro-fused rings. Substituents have been omitted for clarity.

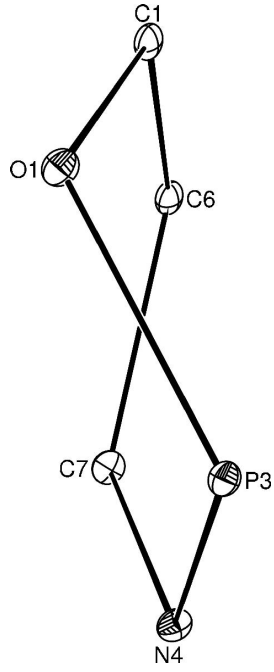


Figure 3
The conformation of the six-membered N/O ring. Substituents have been omitted for clarity.

The reactions of $N_3P_3Cl_6$ with bidentate ligands afford spiro, ansa, bino, dispiro and spiro–ansa phosphazene structures (Dez *et al.*, 1999; Mathew *et al.*, 2000; Tercan, Hökelek, Bilge *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, Dal *et al.*, 2004; Tercan, Hökelek, Işıklan *et al.*, 2004). The reaction of $N_3P_3Cl_6$ with *N*-[(2-hydroxyphenylmethyl)amino]-4,6-dimethylpyridine led to the formation of a novel spirocyclic phosphazene derivative, namely the title compound, (I), instead of ansa or bino phosphazene architectures.

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 0.134 (1) Å (Cremer & Pople, 1975) and a flattened-boat form [Fig. 2; φ = 76.3 (6)° and θ = 106.9 (6)°]. The six-membered P3/O1/C1/C6/C7/N4 ring (*B*) has a total puckering amplitude of 0.605 (3) Å and a twist–boat form [Fig. 3; φ = 11.3(1.4)° and θ = 36.3 (5)°].

In ring *A*, the P—N bond lengths are in the range 1.564 (2)–1.592 (2) Å. The P—N bonds of the phosphazene ring (Table 1) have double-bond character. However, the exocyclic P3—N4 bond [1.657 (2) 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 pair of electrons of atom N4 to the phosphazene ring. The bond angles in ring *A* are comparable with the mean value reported for $N_3P_3Cl_6$, *viz*. 121.4 (3)° (Bullen, 1971).

The close contacts C7···C9 [2.838 (4) Å], H71(C7)···H91(C9) [2.431 (3) Å], H72(C7)···H91(C9) [2.246 (3) Å] and Cl3···H13*A*(C13) [3.075 Å] lead to steric hindrance between the phospazene ring and the bulky spiro-fused substituents, preventing rotation of these groups, as has also been observed in substituted benzene (Ackerman *et al.*, 1969) and imidazole (Hökelek *et al.*, 2002) derivatives having bulky substituents. The dihedral angle between the least-squares planes of the phosphazene and pyridine rings is 80.63 (6)°. Atom P3 is likely to be stereogenic and the absolute configuration, *S*, has been confirmed by refinement of the Flack (1983) parameter.

As can be seen from the packing diagram (Fig. 4), the molecules of (I) extend parallel to the *c* axis and are stacked along the *a* axis.

Experimental

A solution of $N_3P_3Cl_6$ (3.73 g, 10.73 mmol) in dry MeCN (100 ml) was slowly added to a solution of *N*-[(2-hydroxyphenylmethyl)amino]-3,6-dimethylpyridine (2.45 g, 10.73 mmol) and NEt_3 (4.48 ml, 32.19 mmol) in dry MeCN (50 ml) with stirring and refluxing at 253 K. After 1 h, the mixture was allowed to reach ambient temperature. The mixture was refluxed for 30 h, the precipitated salts filtered off and the solution evaporated under reduced pressure. The residue was chromatographed (silica gel 60 g, eluent CH_2Cl_2–*n*-hexane 3:1) and crystallized from tetrahydrofuran/light petroleum (1:1) (m.p. 501 K; yield 3.89 g, 72%).

Crystal data

$C_{14}H_{14}Cl_4N_5OP_3$
M_r = 503.01
Orthorhombic, $P2_12_12_1$
a = 7.9310 (5) Å
b = 11.9091 (10) Å
c = 21.3948 (15) Å
V = 2020.8 (3) Å^3
Z = 4
D_x = 1.653 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5847 reflections
θ = 1.7–27.2°
μ = 0.84 mm^{-1}
T = 100 (2) K
Block, colourless
0.35 × 0.28 × 0.20 mm

Data collection

Stoe IPDS-II diffractometer
φ scans
Absorption correction: integration (*X-RED*; Stoe & Cie, 2002)
T_{min} = 0.758, T_{max} = 0.850
9087 measured reflections
4149 independent reflections
3874 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 27.1°
$h = -6 \rightarrow 10$
$k = -14 \rightarrow 15$
$l = -26 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.074
S = 0.98
4149 reflections
276 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}
Absolute structure: Flack (1983), with 1667 Friedel pairs
Flack parameter: 0.06 (6)

Table 1
Selected geometric parameters (Å, °).

P1—N1	1.584 (2)	P3—O1	1.5875 (17)
P1—N3	1.5643 (19)	P3—N2	1.584 (2)
P2—N1	1.579 (2)	P3—N3	1.592 (2)
P2—N2	1.5743 (19)	P3—N4	1.657 (2)
N3—P1—N1	119.42 (12)	N2—P3—N4	112.83 (11)
N2—P2—N1	120.52 (11)	N3—P3—N4	111.85 (12)
O1—P3—N3	107.80 (10)	P2—N1—P1	118.89 (13)
O1—P3—N4	101.54 (9)	P2—N2—P3	121.04 (14)
N2—P3—O1	104.94 (11)	P1—N3—P3	122.09 (13)
N2—P3—N3	116.38 (11)		
N3—P1—N1—P2	−3.4 (2)	O1—P3—N2—P2	−130.47 (14)
N1—P1—N3—P3	−7.6 (2)	N3—P3—N2—P2	−11.4 (2)
N2—P2—N1—P1	6.7 (2)	N4—P3—N2—P2	119.84 (15)
N1—P2—N2—P3	1.0 (2)	N2—P3—N3—P1	14.8 (2)

Methyl H atoms were positioned geometrically at a distance of 0.96 Å from the parent C atoms; a riding model was used during the refinement process and the U_{iso}(H) values were constrained to be $1.5U_{eq}$(carrier atom). The other H atoms were located in a difference synthesis and refined isotropically [Csp^2—H = 0.86 (4)–0.97 (3) Å, Csp^3—H = 0.91 (4)–0.97 (3) Å and U_{iso}(H) = 0.013 (7)–0.046 (11) Å^2].

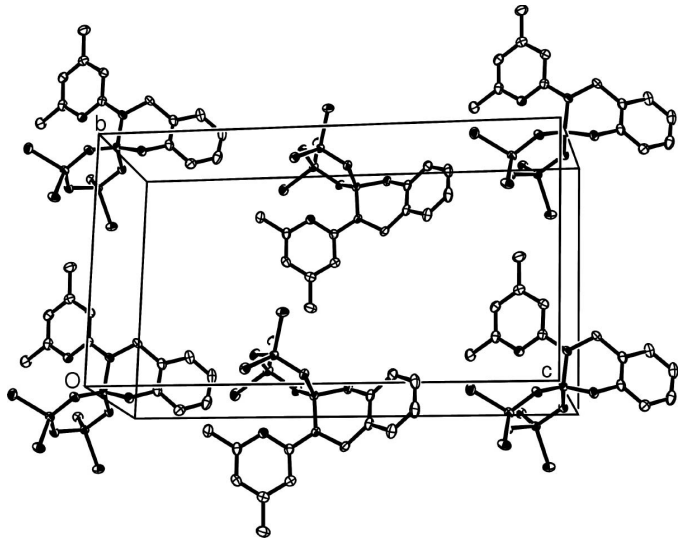


Figure 4
A packing diagram for (I). H atoms have been omitted.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the Stoe IPDS-II diffractometer (purchased under grant F.279 of the University Research Fund), the Commission of Scientific Research Projects of Anadolu University (grant No. 031032) and the Scientific Research Unit of Hacettepe University, (grant No. 02 02 602 002).

References

Ackerman, J. H., Laidlaw, G. M. & Synder, G. A. (1969). *Tetrahedron Lett.* **10**, 3879–3882.
Allcock, H. R., Al-Shali, S., Ngo, D. C., Visscher, K. B. & Parvez, M. (1996). *J. Chem. Soc. Dalton Trans.* pp. 2549–2559.
Allcock, H. R., Dembek, A. A., Mang, M. N., Riding, G. H., Parvez, M. & Visscher, K. B. (1992). *Inorg. Chem.* **31**, 2734–2739.
Allcock, H. R. & Kwon, S. (1986). *Macromolecules*, **19**, 1502–1508.
Allcock, H. R., Napierala, M. E., Cameron, C. G. & O'Connor, S. J. M. (1996). *Macromolecules*, **29**, 1951–1956.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Baek, H., Cho, Y., Lee, C. O. & Shon, Y. S. (2000). *Anti Cancer Drugs*, **11**, 715–725.
Beşli, S., Coles, S. J., Davies, D. B., Eaton, R. J., Hursthouse, M. B., Kılıç, A., Shaw, R. A., Çiftçi, G. Y. & Yeşilot, S. (2003). *J. Am. Chem. Soc.* **125**, 4943–4950.
Blonsky, P. M., Shriver, D. F., Austin P. & Allcock, H. R. (1986). *Solid State Ionics*, **18**, 258–264.
Brandt, K., Kruszynski, R., Bartczak, T. J. & Porwolik-Czomperlik, I. (2001). *Inorg. Chim. Acta*, **322**, 138–144.
Bullen, G. J. (1971). *J. Chem. Soc. A*, pp. 1450–1453.

Coles, S. J., Davies, D. B., Eaton, R. J., Hursthouse, M. B., Kılıç, A., Mayer, T. A., Shaw, R. A. & Yenilmez, G. (2002). *J. Chem. Soc. Dalton Trans.* pp. 365–370.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–13548.
Dembek, A. A., Kim, C., Allcock, H. R., Devine, R. L. S., Shi, Y., Steiner, W. H. & Spangler, C. W. (1991). *Macromolecules*, **24**, 1000–1010.
Dez, I., Mitjaville, J. L., Grützmacher, H., Gramlich, V. & de Jaeger, R. (1999). *Eur. J. Inorg. Chem.* pp. 1673–1684.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hökelek, T., Dinçer, S. & Kılıç, E. (2002). *Cryst. Res. Technol.* **37**, 1138–1142.
Konar, V., Yılmaz, Ö., Öztürk, A.· I, Kırbağ, S. & Arslan, M. (2000). *Bioorg. Chem.* **28**, 214–225.
Mathew, D., Nair, C. P. R. & Ninan, K. N (2000). *Polym. Int.* **49**, 48–56.
Olshavsky, M. A. & Allcock, H. R. (1995). *Macrocycles*, **28**, 6188–6197.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED* (Version 1.04). Stoe & Cie, Darmstadt, Germany.
Tercan, B., Hökelek, T., Bilge, S., Natsagdorj, A., Demiriz, Ş. & Kılıç, Z. (2004). *Acta Cryst.* E**60**, o795–o797.
Tercan, B., Hökelek, T., Dal, H., Süzen, Y. & Kılıç, Z. (2004). *Acta Cryst.* C**60**, o639–o641.
Tercan, B., Hökelek, T., Işıklan, M.,· Ilter, E. E. & Kılıç, Z. (2004). *Acta Cryst.* E**60**, o971–o973.
Uslu, A., Coles, S. J., Davies, D. B., Eaton, R. J., Hursthouse, M. B., Kılıç, A. & Shaw, R. A. (2005). *Eur. J. Inorg. Chem.* pp. 1042–1047.