Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

6′,6′-Dichloro-3,3″-etheno-3,4,3″,4″-tetrahydro-2*H*-1,3-benzoxazine-2-spiro-2′-(2λ^5,4λ^5,6λ^5-cyclotriphosphazene)-4′-spiro-2″-2*H*-1,3-benzoxazine

Barış Tercan,[a] Tuncer Hökelek,[a]* Selen Bilge,[b] Amgalan Natsagdorj,[b] Şemsay Demiriz[b] and Zeynel Kılıç[b]

[a]Hacettepe University, Department of Physics, 06800 Beytepe, Ankara, Turkey, and [b]Ankara University, Department of Chemistry, 06100 Tandoğan, Ankara, Turkey

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

The title compound, $C_{16}H_{16}Cl_2N_5O_2P_3$, a cyclotriphosphazene, has a spiro–ansa–spiro architecture in which the bicyclic system is in the sofa conformation. Two P atoms and one N atom are capable of representing stereogenic centres.

Received 1 April 2004
Accepted 13 April 2004
Online 17 April 2004

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
R factor = 0.057
wR factor = 0.165
Data-to-parameter ratio = 14.1

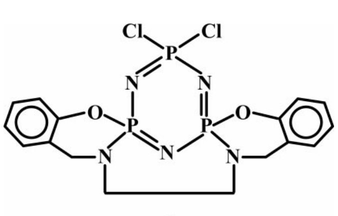
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Trimeric phosphazene, also known as hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, can be considered as the 'standard' compound in the field of phosphazene chemistry (Bullen, 1971). It has potential use in the preparation of many small organocyclophosphazene and polymeric phosphazene derivatives with inorganic skeletons and various side groups (Allcock *et al.*, 1992; Allen, 1994).

In the reactions of $N_3P_3Cl_6$ with bidentate ligands, *e.g.* diols and diamines, four possible reaction pathways have been observed: (i) replacement of two geminal Cl atoms to give spiro derivatives, (ii) replacement of two non-geminal Cl atoms to give ansa derivatives, (iii) intermolecular reactions between Cl atoms of phosphazene rings to give bino derivatives or (iv) intermolecular condensation reactions to yield cyclolinear or cyclomatrix polymers (Dez *et al.*, 1999; Mathew *et al.*, 2000).

To the best of our knowledge, until now the reactions of $N_3P_3Cl_6$ with N_2O_2-donor type aminopodands (tetradentate ligands) have only been investigated by our group (Bilge *et al.*, 2004). The reactions of $N_3P_3Cl_6$ with 2-[({2-[(2-hydroxybenzyl)amino]ethyl}amino)methyl]phenol (Bilge *et al.*, 2004) in dry tetrahydrofuran afford both spiro–ansa–spiro and spiro–bino–spiro architectures. The title compound, (I), is the first example of a spiro–ansa–spiro phosphazene derivative.



(I)

Fig. 1 shows the molecular structure of (I), with the atomic numbering scheme. The phosphazene ring (*A*) is not planar, with a total puckering amplitude of Q_T = 1.684 (15) Å (Cremer & Pople, 1975). Atoms N1, N2 and N3 are displaced from the plane through the P atoms by 0.044 (6), 0.558 (5) and 0.033 (6) Å, respectively. As expected, benzene rings *B* (C1–C6) and *F* (C11–C16) are planar. Ring *C* (P3/O1/C1/C6/C7/N4), ring *D* (P3/N4/C8/C9/N5/P2/N2) and ring *E* (P2/O2/C16/C11/C10/N5) are not planar, with total puckering amplitudes (Cremer & Pople, 1975) of 0.462 (5), 0.735 (6) and 0.471 (7) Å,

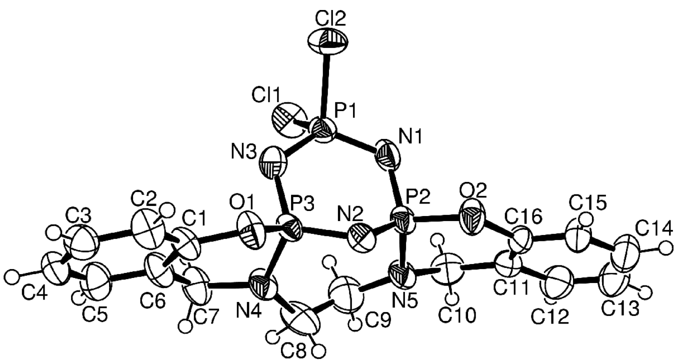


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

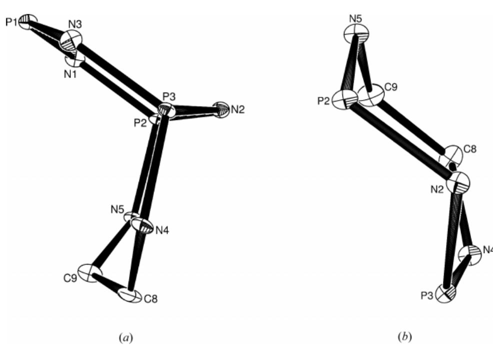


Figure 2
The conformations of (*a*) the bicyclic system and (*b*) ring *D* in (I). The substituents have been omitted for clarity.

respectively. The bicyclic system made up of rings *A* and *D* is in a sofa conformation (Fig. 2*a*). This bicyclic system resembles the very stable 'adamantane' structure. Each ring is V-shaped, with one of the two halves (P2/N1/P1/N3/P3) being essentially planar, while the other half (P2/N5/C9/C8/N4/P3) is not. The dihedral angle between the least-squares planes P2/N1/P1/N3/P3 and P2/P3/N4/N5 is 68.0 (2)°; this can be compared with the reported values of 62.2 (2) and 62.3 (2)° in the bicyclic phosphazene, $[N_4P_4(NC_4H_8)_5(NH^nPr)(N^nPr)]$ (Öztürk *et al.*, 2002).

In the bicyclic system, the maximum separations between P and C atoms are P1···C9 = 3.893 (4) Å and P1···C8 = 4.240 (4) Å. All P···P distances are in the range 2.658 (2)–2.738 (2) Å. The sums of the bond angles around atoms N4 and N5 (356.8 and 346.6°) show a change in the hybridization of atom N5 from trigonal planar towards pyramidal. Thus, atom N5 may represent a stereogenic centre. The planarity of N4 and the pyramidality of N5 especially may depend on the conformation of ring *D* (Fig. 2*b*). Furthermore, atoms P2 and P3 each have four different attachments and thus are also expected to be stereogenic.

In the phosphazene ring, the P—N bond lengths are in the range 1.554 (5)–1.621 (6) Å and exhibit a regular variation with the distance from P1: P1—N1 ≃ P1—N3 < P3—N2 ≃ P2—N2 < P3—N3 ≃ P2—N1. The phosphazene ring P—N bonds (Table 1) show double-bond character. However, P3—N4 [1.613 (5) Å] and P2—N5 [1.648 (5) Å] are at the lower limit of the single-bond length. In phosphazene derivatives, the 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 shortening in the P3—N4 and P2—N5 bonds may possibly depend on electron release from the N atoms to the phosphazene skeleton.

In the phosphazene ring, the endocyclic angles N2—P3—N3 and N1—P2—N2 [114.8 (3) and 114.4 (3)°] are decreased and the exocyclic angles O1—P3—N4 and O2—P2—N5 [104.0 (3) and 104.4 (2)°] are increased, with increased electron donation and withdrawal by the substituents, relative to the 'standard' compound $N_3P_3Cl_6$ (Bullen, 1971). In the latter compound, the corresponding angles are 118.3, 118.5 and 101.2, 101.6°, respectively. The angles P2—N2—P3, P1—N1—P2 and P1—N3—P3 [114.1 (3), 119.1 (3) and 119.3 (3)°] increase with increasing electron supply to the N_3P_3 ring (Kılıç *et al.*, 1996). They are all smaller than the average 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

K_2CO_3 (3.00 g, 22.0 mmol) was added to a stirred solution of 2-[({2-[(2-hydroxybenzyl)amino]ethyl}amino)methyl]phenol (3.00 g, 11.0 mmol) in dry THF (200 ml). The mixture was refluxed for 2 h and then cooled. A solution of $N_3P_3Cl_6$ (1.90 g, 5.50 mmol) in dry THF (75 ml) was added dropwise to the stirred mixture at 263 K over a period of 1 h. After the mixture had been allowed to reach ambient temperature, it was stirred for a further 23 h, with argon passing over the reaction mixture. The precipitated amine hydrochloride and excess of K_2CO_3 were filtered off and the solvent was evaporated under reduced pressure. The residue was dissolved in a dichloromethane–benzene mixture (5:1) and subjected to column chromatography [silica gel: 30 g, eluant: dichloromethane–benzene (5:1)], then crystallized from dichloromethane–*n*-heptane (4:1) (m.p. 553 K; yield 0.55 g, 21%).

Crystal data

$C_{16}H_{16}Cl_2N_5O_2P_3$	D_x = 1.609 Mg m^{-3}
M_r = 474.15	Mo *Kα* radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
a = 15.8433 (12) Å	*θ* = 10–18°
b = 6.6557 (14) Å	*μ* = 0.60 mm^{-1}
c = 20.1339 (10) Å	*T* = 293 (2) K
β = 112.814 (5)°	Rod, colourless
V = 1957.0 (5) Å^3	0.40 × 0.15 × 0.10 mm
Z = 4	

Data collection

Enraf–Nonius CAD-4 diffractometer	θ_{max} = 25.8°
Non-profiled *ω* scans	*h* = 0 → 19
Absorption correction: none	*k* = −8 → 0
3747 measured reflections	*l* = −24 → 22
3559 independent reflections	3 standard reflections
1687 reflections with $I > 2\sigma(I)$	frequency: 120 min
R_{int} = 0.038	intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.165$
$S = 0.98$
3559 reflections
253 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0823P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.83$ e Å^{-3}
$\Delta\rho_{min} = -0.73$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P3—N2	1.588 (5)	P2—N2	1.579 (5)
P3—O1	1.590 (4)	P2—N1	1.621 (6)
P3—N3	1.602 (5)	P2—N5	1.648 (5)
P3—N4	1.613 (5)	O2—C16	1.413 (6)
P1—N1	1.554 (5)	O1—C1	1.406 (7)
P1—N3	1.564 (5)	C10—N5	1.480 (8)
P1—Cl2	2.008 (2)	N4—C8	1.454 (8)
P1—Cl1	2.026 (2)	N4—C7	1.475 (7)
P2—O2	1.574 (4)	N5—C9	1.450 (9)
N2—P3—O1	108.9 (3)	N1—P2—N5	112.3 (3)
N2—P3—N3	114.8 (3)	C16—O2—P2	123.8 (4)
O1—P3—N3	105.9 (3)	C1—O1—P3	118.3 (4)
N2—P3—N4	109.7 (3)	P2—N2—P3	114.1 (3)
O1—P3—N4	104.0 (3)	P1—N1—P2	119.1 (3)
N3—P3—N4	112.8 (3)	P1—N3—P3	119.3 (3)
N1—P1—N3	119.9 (3)	N5—C10—C11	110.2 (6)
N1—P1—Cl2	108.4 (2)	C8—N4—C7	117.7 (5)
N3—P1—Cl2	109.3 (2)	C8—N4—P3	123.0 (4)
N1—P1—Cl1	109.6 (2)	C7—N4—P3	116.1 (4)
N3—P1—Cl1	108.1 (2)	C9—N5—P2	118.9 (4)
Cl2—P1—Cl1	99.60 (11)	C10—N5—P2	114.8 (4)
O2—P2—N2	108.0 (3)	N4—C7—C6	112.5 (5)
O2—P2—N1	106.8 (3)	C6—C1—O1	122.9 (5)
N2—P2—N1	114.4 (3)	C2—C1—O1	115.3 (6)
O2—P2—N5	104.4 (2)	C9—C8—N4	125.7 (7)
N2—P2—N5	110.2 (3)	C8—C9—N5	121.3 (7)
N2—P2—O2—C16	138.6 (5)	C10—C11—C16—O2	−2.4 (10)
N5—P2—O2—C16	21.3 (5)	P2—O2—C16—C11	3.3 (8)
N2—P3—O1—C1	−158.6 (4)	C8—N4—C7—C6	157.8 (6)
N4—P3—O1—C1	−41.7 (5)	P3—N4—C7—C6	−41.9 (7)
O2—P2—N2—P3	166.1 (3)	C1—C6—C7—N4	12.2 (9)
N5—P2—N2—P3	−80.5 (4)	C7—C6—C1—O1	0.1 (10)
O1—P3—N2—P2	−165.5 (3)	P3—O1—C1—C6	17.7 (8)
C16—C11—C10—N5	−26.6 (10)	C7—N4—C8—C9	123.1 (8)
O1—P3—N4—C8	−145.9 (5)	P3—N4—C8—C9	−35.7 (10)
O1—P3—N4—C7	54.9 (5)	N4—C8—C9—N5	69.7 (11)
C11—C10—N5—C9	−165.1 (6)	C10—N5—C9—C8	163.0 (7)
C11—C10—N5—P2	54.2 (8)	P2—N5—C9—C8	−58.1 (9)
O2—P2—N5—C9	171.1 (5)		

Atoms H101 and H102 were located in a difference synthesis and refined isotropically, with C—H = 0.88 (6) and 0.97 (7) Å, respectively. The remaining H atoms were positioned geometrically at distances of 0.93 (Csp^2—H) and 0.97 Å (Csp^3—H) from the carrier atoms; a riding model was used during the refinement process. The U_{iso} values were constrained to be $1.2U_{eq}$ of the carrier atom.

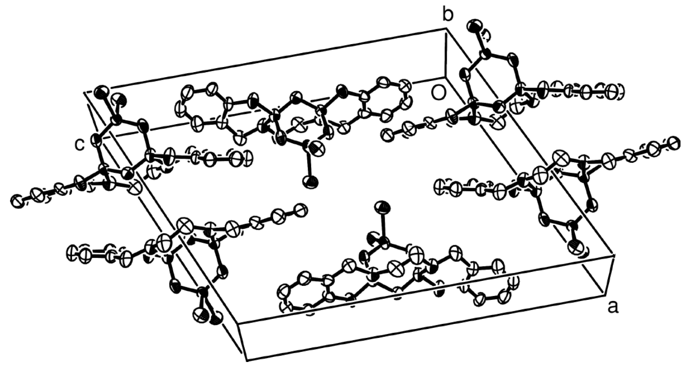


Figure 3
Packing diagram of (I). H atoms have been omitted.

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).

The authors acknowledge the purchase of the CAD-4 diffractometer and the financial support of this work under grants DPT/TBAG1 of the Scientific and Technical Research Council of Turkey and Ankara University, Scientific Research Unit (grant number BAP-2001–07–05–064).

References

Allcock, H. R., Dembek, A. A., Mang, M. N., Riding, G. H., Parvez, M. & Visscher, K. B. (1992). *Inorg. Chem.* **31**, 2734–2739.
Allen, C. W. (1994). *Coord. Chem. Rev.* **31**, 137–173.
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.
Bilge, S., Natsagdorj, A., Demiriz, Ş., Çaylak, N., Kılıç. Z. & Hökelek, T. (2004). *Helv. Chim. Acta.* Submitted.
Bullen, G. J. (1971). *J. Chem. Soc. B*, pp. 1450–1453.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Dez, I., Mitjaville, J. L., Grützmacher, H., Gramlich, V. & de Jaeger, R. (1999). *Eur. J. Inorg. Chem.* pp. 1673–1684.
Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Harms, K. & Wocadlo, S. (1995). XCAD4. University of Marburg, Germany.
Kılıç, A., Begeç, S., Çetinkaya, B., Hökelek, T., Kılıç. Z., Gündüz, N. & Yıldız, M. (1996). *Heteroatom Chem.* **7**, 249–256.
Mathew, D., Nair, C. P. R. & Ninan, K. N. (2000). *Polym. Int.* **49**, 48–56.
Öztürk, L., Işıklan, M., Kılıç. Z. & Hökelek, T. (2002). *Acta Cryst.* C**58**, o80–o83.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.