Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Conformational polymorphism in a chiral spiro-*cis*-*ansa*-bridged cyclotriphosphazene derivative

Simon J. Coles,[a]* David B. Davies,[b] Michael B. Hursthouse,[a] Hanıfe Ibişoğlu,[c] Adem Kılıç[c] and Robert A. Shaw[b]

[a]Department of Chemistry, University of Southampton, Southampton SO17 1BJ, England, [b]Department of Chemistry, Birkbeck College (University of London), Gordon House, 29 Gordon Square, London WC1H 0PP, England, and [c]Gebze Institute of Technology, PK 141, 41400, Gebze/Kocaeli, Turkey
Correspondence e-mail: s.j.coles@soton.ac.uk

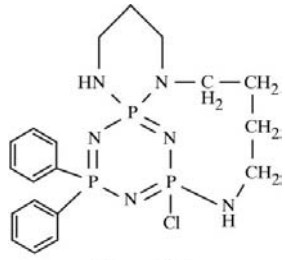
Received 12 October 2001
Accepted 18 October 2001
Online 22 December 2001

The reaction of spermidine with 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazene produces a mixture of products of which one of the fractions is a spiro-*cis*-*ansa* derivative, namely 12-chloro-14,14-diphenyl-2,6,11,13,15,16-hexaaza-1,12-diphosphatricyclo[10.3.1.0^{1,6}]hexadeca-12,14-diene, $C_{19}H_{26}ClN_6P_3$. Recrystallization of this fraction from different solvents results in the formation of two different crystalline forms. The rod morphology formed in dichloromethane–*n*-hexane (1:1) produces a triclinic structure with three molecules in the asymmetric unit. These three molecules adopt different conformations as a result of two NH groups flipping in an *ansa*-bridged ring system. The plate morphology crystals, grown in dichloromethane–*n*-hexane–ethyl acetate (1:1:1), produce a *C*-centred monoclinic structure that adopts a conformation that is essentially the same as one of the forms in the triclinic structure.

Comment

As part of our investigations into the chiral properties of cyclophosphazenes and, in particular, that of configurational isomers, we have investigated the reaction of 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazene with spermine and spermidine. The single-bridged derivatives arising from the reaction with spermine have been demonstrated to be a 50:50 mixture of *meso* and racemic forms (Coles *et al.*, 2002). The analogous reaction with spermidine is expected to give rise to two racemates, which have been observed by ^{31}P NMR, but, so far, have not been separated. Another product from this reaction is a fused tricyclic system (see *Scheme* below) based on a single trimer unit, which is the subject of the present study as it has given rise to different polymorphic forms.

Polymorphism in cyclophosphazene chemistry has hitherto been confined to tetrameric, N_4P_4, or higher ring systems. A review article (Shaw, 1978) mentions tetrameric and pentameric derivatives. The first and probably the best known are the K- (Hazekamp *et al.*, 1962) and T- (Wagner & Vos, 1968) forms of $N_4P_4Cl_8$, which differ in the shape of the eight-membered N_4P_4 ring. Protonated cationic tetramer species, $(N_4HP_4Me_8)_2CoCl_4$, display two types of eight-membered-ring conformations in the same unit cell (Trotter & Whitlow, 1970). Three different crystalline modifications of the pentameric fluoride, $N_5P_5F_{10}$, have been reported, two of which have had their structures determined (Hartsuiker & Wagner, 1978). The acyclic cation $(Ph_3P{=}NPPh_3)^+$, often favoured to stabilize complex inorganic and organometallic anions, displays a variety of P—N—P bond angles. In one structure, both bent and linear forms have been observed in the same asymmetric unit (Wilson & Bau, 1974).



(I) and (II)

We now report the first example of polymorphism involving a trimer N_3P_3 structure. Unlike the other examples of polymorphism referred to above, this is not a function of the NP skeleton. The backbone of the structures presented [Figs. 1, 2, 3 and 4 for molecules (I*a*), (I*b*), (I*c*) and (II*a*) found in the structures of (I) and (II), respectively] is the cyclic N_3P_3 cyclotriphosphazene moiety. The driving force behind this polymorphic behaviour is the conformation of two NH groups, which are part of a nine-membered *cis*-*ansa* moiety linked to a six-membered bis-amino ring bonded to two P atoms of the N_3P_3 ring. The conformation of the NH moieties is determined by the chiral nature of the P atoms to which they are bonded. An inversion of chirality about these atoms necessitates a

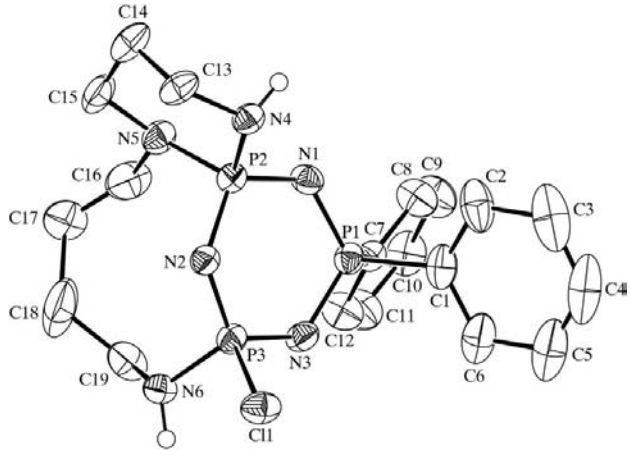


Figure 1
View of molecule (I*a*) in the structure of (I), shown with 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

 DOI: 10.1107/S010827010101770X

flipping of the NH group and as a result there are differing molecular conformations in the two crystal structures presented.

As the conformational arrangements of these molecules are to be compared, their structures will be discussed simultaneously. Selected geometric parameters for the total of four molecules presented are given in Tables 1 and 2 for structures (I) and (II), respectively. The bond lengths and angles in all four molecules conform to expected values derived from structures found in the Cambridge Structural Database (Allen & Kennard, 1993; Orpen *et al.*, 1992). The asymmetric unit of (I) comprises three independent molecules, each exhibiting different conformational forms. Molecules (I*a*), (I*b*) and (I*c*) in (I) are depicted in Figs. 1, 2 and 3, respectively, whilst the structure of (II) [molecule (II*a*)] is presented in Fig. 4.

The structures of (I) and (II) exhibit the same connectivity yet crystallize in different space groups, indicating that they are polymorphic in nature. Molecules (I*a*), (I*c*) and (II*a*) all have the same chirality, *i.e.* *R* about atoms P2/P3, P8/P9 and P2/P3, whilst molecule (I*b*) has *S* chirality for atoms P5 and P6. The conformations of the primary amine groups, and hence those of the ring systems of which they are components, are best described and compared using the torsion angles given in Tables 1 and 2. The conformation of molecule (I*a*) may be assigned as the α form and is described by the torsion angles C13—N4—P2—N1, C16—N5—P2—N1, C16—C17—C18—C19 and C19—N6—P3—N3. Molecule (I*b*) has torsion angles (C32—N10—P5—N7, C35—N11—P5—N7, C35—C36—C37—C38 and C38—N12—P6—N9) similar in magnitude but opposite in sign, indicating an inverted conformation to that of the α form arising from the alternative chirality adopted by P5 and P6. Hence, the *R*/*R* racemate generated through the centre of symmetry in the space group would exhibit essentially the same form as that of (I*a*), the α form. The β form exhibited by molecule (I*c*) [characterized by torsion angles C51—N16—P8—N13, C54—N17—P8—N13, C54—C55—C56—C57 and C57—N18—P9—N15] is similar to that of the α form, apart from the conformation of the N18—P9 bond, which has a torsion angle that is more than 100° larger in magnitude. Molecule (II*a*) has the same numbering scheme as that of molecule (I*a*) and is hence characterized by the same

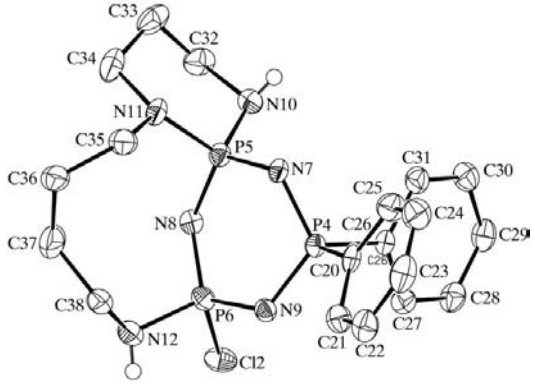


Figure 2
View of molecule (I*b*) in the structure of (I), shown with 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

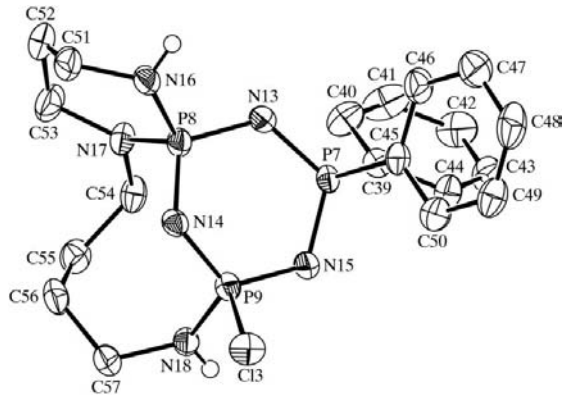


Figure 3
View of molecule (I*c*) in the structure of (I), shown with 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

torsion angles. Comparison of these angles shows it to be essentially the α form. From puckering analysis (Cremer & Pople, 1975), the conformations of the spiro-P—N—C—C—C—N rings are shown to be those of a boat; however, in the case of molecule (I*b*), the apical atoms (P5 and C33) are opposite in orientation to those of the other molecules, which is due to the inversion in chirality about P5. The conformations adopted by the nine-membered rings may be compared using the torsion angles described in Tables 1 and 2 [C16—C17—C18—C19, C35—C36—C37—C38, C54—C55—C56—C57 and C16—C17—C18—C19 for molecules (I*a*), (I*b*), (I*c*) and (II*a*) respectively]. From these values, it can be seen that (I*a*) and (II*a*) adopt a similar α conformation [inverted in (I*b*) as a result of the chirality inversion], whereas the conformation is more distorted in (I*c*), *i.e.* the β form.

The behaviour described above has implications for the conformation of the cyclophosphazene ring system, which one would normally expect to be planar. Puckering analysis (Cremer & Pople, 1975) shows the N_3P_3 ring in (I*a*) to be a boat, whilst the remaining molecules exhibit a twist-boat conformation. The deviations from planarity are not great, but nevertheless significant [maximum deviations: molecule (I*a*) =

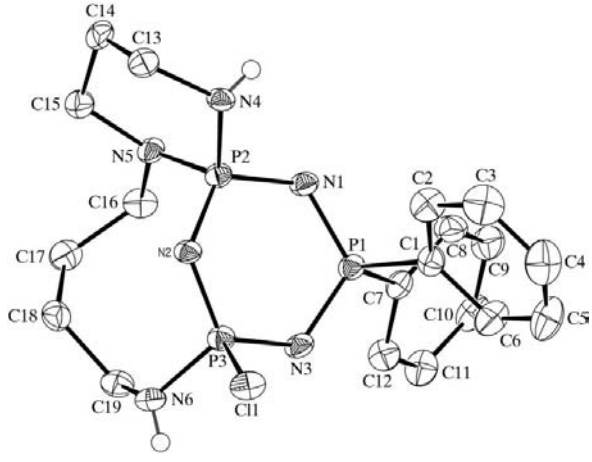


Figure 4
View of the molecular structure of (II), molecule (II*a*), shown with 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

0.133 Å (P1), (I*b*) = 0.259 Å (P4), (I*c*) = 0.221 Å (N14) and (II*a*) = 0.181 Å (P1)]. The smaller deviations in the α form with respect to that of the β form indicate that less strain on the system is induced by this arrangement. This is not accompanied by a decrease of the P···P non-bonded distance, as has been observed in similar, but shorter, *ansa*-bridged N_3P_3 systems (Contractor *et al.*, 1986), because the P···P cross-ring separations are comparable to those observed in unstrained N_3P_3-containing structures (Contractor *et al.*, 1986).

Experimental

A solution of 2,2,4,4-tetrachloro-6,6-diphenylcyclotriphosphazene (7.24 g, 0.0168 mol) in a 200 ml mixture of Et_2O and *n*-hexane (3:5) was added dropwise to a stirred solution of triethylamine (5.10 g, 0.05049 mol) in 200 ml of the same solvent mixture and then spermidine (2.39 g, 0.0168 mol) in 50 ml of the same solvent mixture was added. The reaction mixture was stirred under an atmosphere of argon at room temperature for 22 d. Triethylamine hydrochloride was filtered off and the solvent removed under reduced pressure at 303 K. Two compounds were detected [R_F = 0.9 (product 1) and 0.36 (product 2)] by thin-layer chromatography using dichloromethane–ethyl acetate (3:1) as the mobile phase. These were separated by column chromatography on silica gel using dichloromethane–ethyl acetate (1:1) as eluent. The isomeric mixture of the singly bridged compound (product 1) was obtained as a colourless solid (m.p. 331–341 K, 2.5 g, yield 13.23%), and the fused tricyclic derivative (product 2), the title compound, was initially crystallized from dichloromethane–*n*-hexane (1:1) (m.p. 449 K, 0.8 g, yield 10%) to give structure (I) and then from DCM–ethyl acetate–*n*-hexane (1:1:1) to give structure (II). Found (product 2): C 48.8, H 5.10, N 18.00%; M^+ 467.1; $C_{19}H_{26}ClN_6P_3$ requires: C 48.89, H 5.61, N 18.00%; *M* 466.8.

Compound (I)

Crystal data

$C_{19}H_{26}ClN_6P_3$
M_r = 466.82
Triclinic, $P\overline{1}$
a = 10.083 (2) Å
b = 12.770 (3) Å
c = 25.816 (5) Å
α = 95.64 (3)°
β = 96.98 (3)°
γ = 92.07 (3)°
V = 3279.5 (11) Å^3
Z = 6
D_x = 1.418 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 21 067 reflections
θ = 2.9–27.5°
μ = 0.41 mm^{-1}
T = 120 (2) K
Rod, colourless
0.18 × 0.08 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
T_{min} = 0.929, T_{max} = 0.980
42 350 measured reflections
14 040 independent reflections
8616 reflections with $I > 2\sigma(I)$
R_{int} = 0.071
θ_{max} = 27.5°
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = -33 \rightarrow 33$

Refinement

Refinement on F^2
$R(F)$ = 0.059
$wR(F^2)$ = 0.158
S = 1.06
14 040 reflections
807 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0724P)^2 + 0.3311P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.081
$\Delta\rho_{max}$ = 1.28 e Å^{-3}
$\Delta\rho_{min}$ = −1.25 e Å^{-3}

Table 1
Selected torsion angles (°) for (I).

C13—N4—P2—N1	−159.13 (17)	C35—N11—P5—N7	−56.87 (18)
C16—N5—P2—N1	−67.88 (18)	C38—N12—P6—N9	67.57 (19)
C19—N6—P3—N3	60.1 (2)	C54—C55—C56—C57	84.5 (3)
C16—C17—C18—C19	43.6 (3)	C51—N16—P8—N13	−148.6 (2)
C35—C36—C37—C38	64.2 (4)	C54—N17—P8—N13	−68.46 (19)
C32—N10—P5—N7	−158.18 (15)	C57—N18—P9—N15	165.9 (2)

Compound (II)

Crystal data

$C_{19}H_{26}ClN_6P_3$
M_r = 466.82
Monoclinic, *C*2/*c*
a = 16.163 (3) Å
b = 16.298 (3) Å
c = 17.401 (4) Å
β = 103.36 (3)°
V = 4459.7 (15) Å^3
Z = 8
D_x = 1.391 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10 998 reflections
θ = 2.9–27.5°
μ = 0.41 mm^{-1}
T = 120 (2) K
Plate, colourless
0.20 × 0.10 × 0.01 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
T_{min} = 0.923, T_{max} = 0.998
20 266 measured reflections
5053 independent reflections
3119 reflections with $I > 2\sigma(I)$
R_{int} = 0.125
θ_{max} = 27.5°
$h = -20 \rightarrow 20$
$k = -21 \rightarrow 21$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R(F)$ = 0.054
$wR(F^2)$ = 0.125
S = 0.99
5053 reflections
271 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Table 2
Selected torsion angles (°) for (II).

C16—C17—C18—C19	−67.4 (4)	C16—N5—P2—N1	57.2 (2)
C13—N4—P2—N1	157.3 (2)	C19—N6—P3—N3	−64.9 (2)

For both structures, the amino H atoms were found experimentally from a difference map and freely refined, whilst the remaining H atoms were located in idealized positions (C—H = 0.95 and 0.99 Å) with their displacement parameters riding on those of the parent atom. The *ansa*-bridged rings in molecules (I*a*) and (I*b*) exhibit positional disorder about atoms C17 and C36 (50 and 75% site occupation, respectively). Both components were constrained to idealized methylene bond lengths with isotropic displacement parameters.

For both compounds, data collection: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990).

The authors would like to thank the EPSRC for funding of crystallographic facilities and Gebze Institute of Technology Research Fund for partial financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1540). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–429.
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.* In the press.
Contractor, S. R., Hursthouse, M. B., Parkes, H. G., Shaw, L. S. (nee Gozen), Shaw, R. A. & Yilmaz, Y. (1986). *Phosphorus Sulfur*, **28**, 267–275.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Hartsuiker, J. G. & Wagner, A. J. (1978). *J. Chem. Soc. Dalton Trans.* pp. 1425–1430.
Hazekamp, R., Migchelsen, T. & Vos, A. (1962). *Acta Cryst.* **15**, 539–543.
Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1992). *International Tables for Crystallography*, Vol. C. Dordrecht: Kluwer Academic Publishers.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.
Shaw, R. A. (1978). *Phosphorus Sulfur*, **4**, 101–121.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Trotter, J. & Whitlow, S. H. (1970). *J. Chem. Soc. A*, pp. 460–464.
Wagner, A. J. & Vos, A. (1968). *Acta Cryst.* B**24**, 707–713.
Wilson, R. D. & Bau, R. (1974). *J. Am. Chem. Soc.* **96**, 7601–7602.