Hanekamp, J. C. (1992). PhD thesis, University of Utrecht, The Netherlands.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sluis, P. van der & Spek, A. L. (1990). *Acta Cryst.* A**46**, 194–201.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Spek, A. L. (1994). *Am. Crystallogr. Assoc. Abstr.* **22**, 66.
Spek, A. L. (1997). *HELENA. Program for Data Reduction*. University of Utrecht, The Netherlands.
Spek, A. L., Duisenberg, A. J. M., van den Heuvel, H. L. A., Boer Rookhuizen, R. & Bosch, R. (1990). *Acta Cryst.* C**46**, 630–631.

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trans-2,6-Bis(ethylamino)-2,4,4,6,8,8-hexamorpholinocyclo-2λ^5, 4λ^5, 6λ^5, 8λ^5-tetraphosphazatetraene

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Abstract

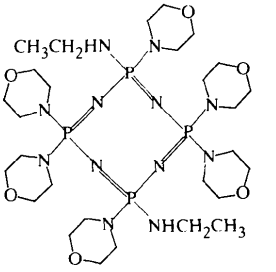
The title compound, $C_{28}H_{60}N_{12}O_6P_4$, consists of a chair-shaped cyclic tetrameric phosphazene ring with six bulky morpholino and two ethylamino side groups. The two ethylamino side groups are in *trans* positions. The bulky substituents are effective in determining the eight-membered-ring conformation. The endocyclic N—P—N angles around the P atoms having different substituents are not the same as the P—N—P angles of the macrocyclic ring.

Comment

Cyclophosphazenes ($N_3P_3Cl_6$ and $N_4P_4Cl_8$) have potential use in the synthesis of new high polymeric phosphazenes with inorganic backbones, which have many different uses (Allcock, 1985; Hökelek & Kılıç, 1990; Hökelek *et al.*, 1996). The small-molecule organo–cyclophosphazenes are also small-molecule models for the corresponding linear organo–polyphosphazenes (Allcock, 1985). Some of the aminophosphazenes are thought to be useful as cancer chemotherapeutic agents (Chernov *et al.*, 1959; van der Huizen, 1984). A relationship is observed between the structures of the cyclophosphazenes and cytostatic activity (van der Huizen, 1984), and for effective tumour growth inhibition, electron-donating groups (*e.g.* aziridine, pyrrolidine and morpholine) in the P–N ring skeleton appear to be essential.

There are two crystal modifications, *K* and *T* forms, of $N_4P_4Cl_8$, which is known as a standard compound for tetrameric phosphazenes (Hazekamp *et al.*, 1962; Wagner & Vos, 1968). The crystal structures of some $N_4P_4Cl_8$ derivatives, such as *β-trans*-$N_4P_4(NHMe)_4Ph_4$ (Bullen & Mallinson, 1972), $N_4P_4Cl_4(NEt_2)_4$ (Hökelek & Kılıç, 1990), $N_4P_4(NMe_2)_8$ (Bullen, 1962) and $N_4P_4Cl_7(OC_6H_2\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}Me)$ (Hökelek *et al.*, 1996), have been determined.

A structure analysis of the title compound, (I), was undertaken to determine the influences of the relatively hindered side groups, and also of steric and electronic factors, on the macrocyclic tetraphosphazene ring. The title compound is illustrated in Fig. 1. Its structure consists of a cyclic tetrameric phosphazene ring in a chair conformation with two ethylamino (in 2,6-*trans* positions) and six bulky morpholino side groups. The four P atoms are coplanar and the four N atoms are displaced above (+) and below (−) their plane by equal amounts [N1 −0.380 (5) and N2 0.555 (4) Å]. The conformation of the macrocyclic phosphazene ring is indicated by the torsion angles of the ring bonds in



(I)

which the symmetry operation reverses the sign of a torsion angle (shown in Fig. 2). From the distribution of the endocyclic torsion angles, it appears that in the central ring there are two local pseudo-mirrors, one running along the midpoints of the N1—P1 and N1′—P1′ bonds, the other along the midpoints of the P2—N2′ and P2′—N2 bonds.

The P—N—P bond angles are in the range 127.3 (2)–134.4 (2)° [average 130.9 (2)°]. Similar spreads of P—N—P angles were observed in *β-trans*-$N_4P_4Cl_4(NMe_2)$ (Hökelek & Kılıç, 1990) and $N_4P_4Cl_7(OC_6H_2\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}Me)$ (Hökelek *et al.*, 1996), and it was reported that such large angles appear to be characteristic of molecules containing chlorine or fluorine (George *et al.*, 1972). Although, the title compound contains neither chlorine nor fluorine, large P—N—P angles appear to be due to the different substituents on the P atoms. The variation in the endocyclic N—P—N bond angles are in the range 117.4 (2)–121.5 (2)° [average 119.5 (2)°]. In $N_3P_3Cl_6$ derivatives, it has been observed that endocyclic (N—P—N) angles about P decrease

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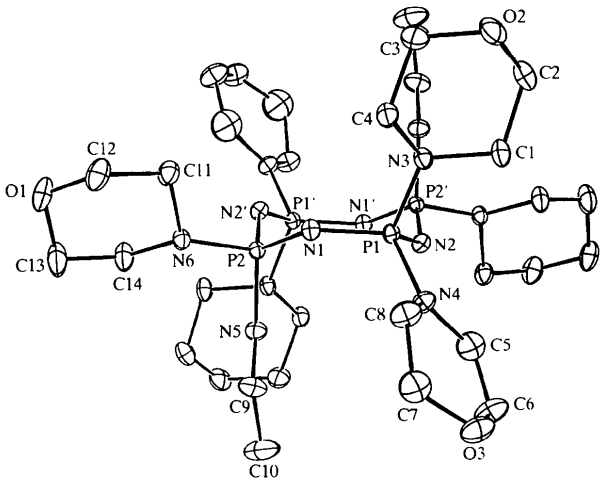

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

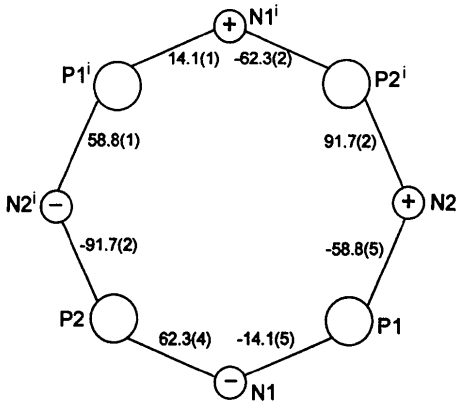

Fig. 2. The shape of the phosphazene ring with torsion angles (°). Symmetry code as in Table 1.

while exocyclic (*R*—P—*R'*) angles increase (Hökelek *et al.*, 1994, 1996). The title compound, (I), and other tetrameric phosphazenes containing bulky groups are different. The exocyclic angle N3—P1—N4 [107.7 (2)°] is highly affected, while the endocyclic angle N1—P1—N2 [121.5 (2)°] is less affected, by the existence of the two repelling morpholino groups bonded to the P1 atom compared with $N_4P_4Cl_8$ (Cl—P—Cl 103.1 and N—P—N 120.5°; Wagner & Vos, 1968). On the other hand, the exocyclic angle N5—P2—N6 [103.5 (2)°] remains unchanged, while the endocyclic angle N1—P2—N2' [117.4 (2)°] decreases as a result of the morpholino and ethylamino groups bonded to the P2 atom. These interactions show that steric factors are more dominant than electronic factors with respect to the ring skeleton. The P1—N2—P2' angle is 134.4 (2)°, but the P1—N1—P2 [127.3 (2)°] angle is narrowed compared with the corresponding angle in $N_4P_4Cl_8$ (133.6 and 137.6°; Wagner & Vos, 1968).

In tetrameric phosphazenes, the P—N bond lengths have been correlated with the electronegativities of the substituents (Bullen & Tucker, 1972). In the present structure, the ethylamino and bulky morpholino are electron-donating groups. The average ring P—N bond length is 1.583 (4) Å, which is smaller than the single P—N bond length of 1.683 (5) Å (Allen *et al.*, 1987). The short bonds in the ring have appreciable double-bond character; this is generally observed for phosphanitrilic molecules (Wagner & Vos, 1968).

Experimental

In this study, compound (I) was prepared from the reaction of morpholine (10.0 g, 116.5 mmol) and *trans*-2,6-$N_4P_4Cl_6(NHEt)_2$ (1.6 g, 3.2 mmol) in chloroform (60 ml). Triethylamine (5.2 g, 51.0 mmol) was added to this mixture, which was worked up according to the literature method of Contractor *et al.* (1987). The compound was crystallized from acetonitrile [m.p. 503–568 K; yield: 2.9 g (59%)].

Crystal data

$C_{28}H_{60}N_{12}O_6P_4$
M_r = 784.75
Triclinic
$P\bar{1}$
a = 9.041 (1) Å
b = 11.242 (1) Å
c = 11.637 (1) Å
α = 65.482 (5)°
β = 66.853 (5)°
γ = 73.376 (5)°
V = 978.75 (17) Å^3
Z = 1
D_x = 1.331 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11–18°
μ = 0.248 mm^{-1}
T = 298 K
Block-like
0.30 × 0.25 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*MolEN*; Fair, 1990)
T_{min} = 0.985, T_{max} = 0.999
4224 measured reflections
3961 independent reflections
2700 reflections with $F > 3\sigma(F)$

R_{int} = 0.063
θ_{max} = 26.3°
$h = -11 \rightarrow 0$
$k = -14 \rightarrow 13$
$l = -14 \rightarrow 13$
3 standard reflections
every 250 reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F
R = 0.073
wR = 0.084
S = 1.07
2700 reflections
216 parameters
H atoms riding
$w = 1/[\sigma(F)^2 + (0.02F)^2 + 1.0]$

$(\Delta/\sigma)_{max}$ = 0.04
$\Delta\rho_{max}$ = 0.83 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

P1—N1	1.583 (4)	P2—N1	1.585 (3)
P1—N2	1.578 (4)	P2—N2'	1.585 (4)
N1—P1—N2	121.5 (2)	P1—N1—P2	127.3 (2)
N1—P2—N2'	117.4 (2)	P1—N2—P2'	134.4 (2)
N3—P1—N1—P2	−138.1 (3)	N6—P2—N1—P1	−176.9 (3)
N4—P1—N1—P2	106.7 (4)	N5—P2—N1—P1	−65.1 (4)
N2—P1—N1—P2	−14.1 (5)		

Symmetry code: (i) $-x, 1-y, -z$.

The title structure was solved by the Patterson method. H-atom positions were calculated geometrically, with U(H) = $1.3U_{eq}$ of the parent non-H atom. A riding model was used in the refinement. Due to the inconsistent values of some of the components of the displacement parameters of the C5 and C7 atoms, they were refined isotropically during the refinement process.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1358). Services for accessing these data are described at the back of the journal.

References

Allcock, H. R. (1985). *Chem. Eng. News*, **63**, 22–36.

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.

Bullen, G. J. (1962). *J. Chem. Soc.* pp. 3193–3203.

Bullen, G. J. & Mallinson, P. R. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1412–1416.

Bullen, G. J. & Tucker, P. A. (1972). *J. Chem. Soc. Dalton Trans.* pp. 2437–2442.

Chernov, V. A., Lytkina, V. B., Sergievskaya, S. I., Kropacheva, A. A., Parshina, V. A. & Sventsitkaya, L. E. (1959). *Farmokol. Toksikol. (Moskow)*, **22**, 365–367; (1960). *Chem. Abstr.* **54**, 7900.

Contractor, S. R., Kılıç, Z. & Shaw, R. A. (1987). *J. Chem. Soc. Dalton Trans.* pp. 2023–2029.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

George, R. D., Mackay, K. M. & Stobart, S. R. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1505–1509.

Hazekamp, R., Migchelsen, T. & Vos, A. (1962). *Acta Cryst.* **15**, 539–543.

Hökelek, T. & Kılıç, Z. (1990). *Acta Cryst.* C**46**, 1519–1521.

Hökelek, T., Kılıç, A., Begeç, S., Kılıç, Z. & Yıldız, M. (1996). *Acta Cryst.* C**52**, 3243–3246.

Hökelek, T., Kılıç, Z. & Kılıç, A. (1994). *Acta Cryst.* C**50**, 453–456.

Huizen, A. A. van der (1984). PhD thesis, University of Gröningen, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Wagner, A. J. & Vos, A. (1968). *Acta Cryst.* B**24**, 707–713.

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Spiro[carbazole-1(2*H*),2′-[1,3]dithiolan]-4(3*H*)-one

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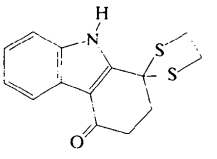
Abstract

The title compound, $C_{14}H_{13}NOS_2$, consists of a carbazole skeleton and a pentacyclic dithiolane ring bonded at position 1. The heteroatoms in the molecule are responsible for the changes in the bond lengths and angles of the carbazole core.

Comment

The title compound is an intermediate in the synthesis of tetracyclic indole alkaloids (Patır, 1995; Patır *et al.*, 1996). It is used as a starting material for the preparation of 4-aminotetrahydrocarbazol-1-one derivatives (Patır & Götz, 1993; Patır *et al.*, 1997). The tricyclic 4-aminotetrahydrocarbazole and 2-chain-substituted 4-oxocarbazole derivatives allow formation of the dasycarpidone skeleton (Magnus *et al.*, 1992). Except for the 4-acetaminotetrahydrocarbazole derivative (Vogel *et al.*, 1982), 4-aminotetrahydrocarbazole has not been isolated in the free form, until now. Recently, starting from the title compound, (I), the stable tricyclic 4-aminotetrahydrocarbazole derivative was isolated in the free form (Patır, 1995; Patır & Götz, 1993). The structure determination of the title compound, (I), was undertaken in order to understand the effects of the dithiolane ring at position 1 on the geometry of the carbazole system and to compare the results obtained with those of 2,3-dihydro-9-(phenylsulfonyl)carbazole-4(1*H*)-one and 1,2,3,4-tetrahydrocarbazole-1-spiro-2′-[1,3]dithiolane (Hökelek *et al.*, 1994).



(I)

The title compound (Fig. 1) consists of a carbazole skeleton and a pentacyclic dithiolane ring spiro-bonded at position 1. The S atoms of the dithiolane