

the two S atoms are related by a center of symmetry with $\theta_i = \theta_j$ [$= 66^\circ$; θ_i and θ_j are spherical polar coordinates specifying the direction of the vector $S_i \cdots S_j$ with respect to the planes $Y_i-S_i-Z_i$ and $Y_j-S_j-Z_j$ (Guru Row & Parthasarathy, 1981)].

Our analysis of coordination geometry around S, Se has shown that of the two lone pairs available for coordination around S and Se, a $p\pi$ type and an sp^2 hybrid type orbital (Boyd, 1978), metal ions choose the $p\pi$ type orbital exclusively for coordination (Rosenfield *et al.*, 1977; Guru Row & Parthasarathy, 1981; Ramasubbu & Parthasarathy, 1987). This electronic preference may be due to the achievement of better overlap between the two interacting orbitals. However, for a particular S- or Se-containing heterocycle, both electronic and steric factors may be important for determining the geometry of monocoordinated metal complexes. For example, by considering the interaction between the axial substituent and the β methylene groups of the ring, Lambert, Mixan & Johnson (1973) have shown that the axial isomer predominates at S whereas both axial and equatorial isomers occur at Se in similar compounds. Several monocoordinated complexes with such bonding have been reported in many crystal structures (Barnes, Hunter & Lown, 1977; Fowler & Griffiths, 1978).

Our analysis of the interaction of S or Se with metal ions in these and other complexes shows that irrespective of axial or equatorial coordination, the metal ions tend to approach S or Se nearly perpendicular to the sulfide or selenide plane with $\theta \approx 20^\circ$ (Rosenfield *et al.*, 1977; Ramasubbu & Parthasarathy, 1987). Since the pz orbital is symmetrical with respect to the sulfide or selenide plane, approaches from above and from below the plane are possible; one may be characterized as

being 'axial' and the other 'equatorial'. However, it is clear that the electrophiles do not approach S or Se in the plane seeking the other lone pair (sp^2 type) at $\theta = 90^\circ$ and $\varphi = 180^\circ$ since this lone pair is not a HOMO (Rosenfield *et al.*, 1977).

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References

- ADDISON, W. E. (1961). *Structural Principles in Inorganic Compounds*, p. 6. New York: John Wiley.
- BARNES, J. C., HUNTER, G. & LOWN, M. W. (1977). *J. Chem. Soc. Dalton Trans.* pp. 458–460.
- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- BOYD, D. B. (1978). *J. Phys. Chem.* **82**, 1407–1416.
- FOWLER, J. M. & GRIFFITHS, A. (1978). *Acta Cryst.* **B34**, 1709–1710; 1711–1712; 1712–1713.
- FRENZ, B. A. (1982). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
- GURU ROW, T. N. & PARTHASARATHY, R. (1981). *J. Am. Chem. Soc.* **103**, 477–479.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL 5138. Oak Ridge National Laboratory, Tennessee, USA.
- LAMBERT, J. B., MIXAN, C. E. & JOHNSON, D. H. (1973). *J. Am. Chem. Soc.* **95**, 4634–4639.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- RAMASUBBU, N. & PARTHASARATHY, R. (1987). *Phosphorus Sulfur*, **31**, 221–229.
- RAMASUBBU, N., PARTHASARATHY, R. & MURRAY-RUST, P. (1986). *J. Am. Chem. Soc.* **108**, 4308–4314.
- ROSENFELD, R. E. JR., PARTHASARATHY, R. & DUNITZ, J. D. (1977). *J. Am. Chem. Soc.* **99**, 4860–4862.

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Structure of a Triclinic Modification of 4,4,4',4',6,6,6',6',8,8,8',8'-Dodecachloro-2,2'-dimethylbi(cyclotetraphosphazene)

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Abstract. $C_2H_6Cl_{12}N_8P_8$, $M_r = 815.35$, triclinic, $P\bar{1}$, $a = 8.436$ (1), $b = 10.005$ (1), $c = 17.153$ (2) Å, $\alpha = 86.19$ (1), $\beta = 80.26$ (1), $\gamma = 108.83$ (1)°, $V = 1339.1$ (3) Å³, $Z = 2$, $D_x = 2.022$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 17.4$ cm⁻¹, $F(000) = 796$, $T = 110$ K, $R = 0.044$ for 4553 observed reflections with

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$I > 2.5\sigma(I)$. The two P–P coupled eight-membered cyclotetraphosphazene rings are in *cis* position, with a P–P bond length of 2.194 (2) Å. Average bond lengths are P(Me)–N = 1.592 (2), P(Cl₂)–N = 1.550 (2) [in a P(Me)–N–P(Cl₂) segment], P(Cl₂)–N = 1.562 (2) [in a P(Cl₂)–N–P(Cl₂) segment], P–C = 1.781 (4) and P–Cl = 2.001 (1) Å.

Introduction. The title compound was obtained as part of a study on the reactivity of octachlorocyclotetraphosphazene (NPCl₂)₄ towards alkyllithium reagents (Winter, 1986). It is formed in a reaction with MeI in THF at 195 K (Winter & van de Gramppe, 1984). Recrystallization from hot petroleum ether yielded a batch with block-shaped crystals and flat needles that turned out to be two modifications of the same compound. The crystal structure of the block-shaped orthorhombic modification will be presented elsewhere. Here we will describe the crystal structure of the needle-shaped triclinic crystals, most of which were found to be macroscopically twinned.

Experimental. Colourless crystals were obtained by recrystallization from petroleum ether. Data were collected (de Boer & Duisenberg, 1984) on an Enraf–Nonius CAD-4F diffractometer (110 K; graphite-monochromated Mo K α radiation; 6443 reflections scanned; $\omega/2\theta$ scan; $\Delta\omega = (0.80 + 0.35 \tan\theta)^\circ$; $1.22 < \theta < 28^\circ$; $h\ 0:11$, $k\ -13:12$, $l\ -22:22$) for a specimen (0.13 × 0.14 × 0.17 mm) that was cut from a twinned needle-shaped crystal. Three reference reflections measured every 2 h of exposure (32 $\bar{1}$: r.m.s.d. 1.8%; 03 $\bar{2}$: r.m.s.d. 1.6%; 106: r.m.s.d. 1.7%) showed no decay during the 68.3 h of X-ray exposure time. Cell dimensions were derived from the setting angles of 22 reflections ($22 < \theta < 23^\circ$). The intensities were corrected for Lorentz and polarization effects and for absorption with the *DIFABS* (Walker & Stuart, 1983) procedure (corrections in the range 0.87 to 1.09). The variance $\sigma^2(I)$ was calculated based on counting statistics plus a term $(PI)^2$, where P (= 0.038) is the instability constant as derived from the excess variance in the reference reflections (McCandlish, Stout & Andrews, 1975). The structure was solved by direct methods with *SHELXS84* (Sheldrick, 1984) and the positions and anisotropic thermal parameters for the non-hydrogen atoms refined with blocked full-matrix least-squares procedures (*SHELX76*; Sheldrick, 1976) minimizing the function $\sum w(|F_o| - |F_c|)^2$. H atoms were located from a difference Fourier map and their positions refined with a common isotropic temperature factor. Convergence was reached at $R = 0.044$, $wR = 0.049$; $w = 1/\sigma^2(F)$; $S = 1.88$; 4553 observed reflections with $I > 2.5\sigma(I)$; 290 refined parameters; $\langle \Delta/\sigma \rangle = 0.01$; maximum $\Delta/\sigma = 0.3$. Minimum and maximum residual densities in the final difference Fourier map are in the range -1.16 to

Table 1. *Final coordinates and equivalent isotropic thermal parameters and their e.s.d.'s in parentheses*

	x	y	z	U_{eq} (Å ²)
Cl(11)	0.8352 (2)	0.0682 (1)	0.24911 (7)	0.0245 (4)
Cl(12)	0.9240 (2)	0.0281 (1)	0.41551 (7)	0.0213 (3)
Cl(13)	0.3888 (1)	0.2347 (1)	0.42610 (7)	0.0218 (3)
Cl(14)	0.5748 (2)	0.1464 (1)	0.55312 (7)	0.0181 (3)
Cl(15)	0.6958 (2)	0.6658 (1)	0.36320 (7)	0.0195 (3)
Cl(16)	0.9677 (1)	0.6815 (1)	0.46699 (7)	0.0177 (3)
Cl(21)	1.3255 (2)	0.9773 (1)	0.07704 (8)	0.0254 (3)
Cl(22)	1.1903 (2)	0.8969 (1)	0.25954 (7)	0.0239 (3)
Cl(23)	0.6532 (2)	0.8229 (2)	0.11796 (9)	0.0322 (4)
Cl(24)	0.9474 (2)	0.8234 (2)	-0.02016 (9)	0.0398 (5)
Cl(25)	0.7026 (2)	0.3046 (2)	0.05531 (8)	0.0364 (4)
Cl(26)	0.6068 (2)	0.3554 (2)	0.22850 (8)	0.0430 (5)
P(11)	1.0914 (1)	0.4674 (1)	0.29693 (7)	0.0122 (3)
P(12)	0.8786 (2)	0.1716 (1)	0.34351 (7)	0.0133 (3)
P(13)	0.6228 (2)	0.2603 (1)	0.44601 (7)	0.0135 (3)
P(14)	0.8324 (1)	0.5521 (1)	0.39903 (7)	0.0119 (3)
P(21)	1.1353 (2)	0.5195 (1)	0.16705 (7)	0.0135 (3)
P(22)	1.1545 (2)	0.8188 (1)	0.15680 (7)	0.0147 (3)
P(23)	0.8434 (2)	0.7451 (1)	0.09482 (9)	0.0238 (4)
P(24)	0.7858 (2)	0.4433 (1)	0.13006 (7)	0.0173 (3)
N(11)	1.0487 (5)	0.3009 (4)	0.3212 (2)	0.0163 (9)
N(12)	0.7053 (5)	0.1887 (4)	0.3804 (2)	0.0160 (9)
N(13)	0.7116 (5)	0.4193 (4)	0.4591 (2)	0.0168 (9)
N(14)	0.9491 (5)	0.5372 (4)	0.3223 (2)	0.0141 (9)
N(21)	1.2153 (5)	0.6888 (4)	0.1485 (2)	0.0174 (9)
N(22)	0.9704 (5)	0.8115 (4)	0.1497 (2)	0.021 (1)
N(23)	0.7604 (7)	0.5812 (5)	0.0963 (4)	0.057 (1)
N(24)	0.9606 (5)	0.4378 (4)	0.1413 (2)	0.0185 (9)
C(11)	1.2881 (6)	0.5569 (5)	0.3261 (3)	0.018 (1)
C(21)	1.2919 (6)	0.4481 (5)	0.1239 (3)	0.020 (1)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

1.78 e Å⁻³ with maxima in the neighbourhood of Cl(24) and Cl(26), indicating some residual disorder in one of the rings. The final values of the refined parameters are given in Table 1.* Scattering factors from Cromer & Mann (1968). Anomalous dispersion from Cromer & Liberman (1970). The programs *PLATON* and *PLUTON* (Spek, 1982) were used for the calculation of geometric data and the preparation of illustrations.

Discussion. Fig. 1 gives a view of the title compound including the adopted numbering scheme. Selected data on the geometry are given in Table 2. The triclinic unit cell contains two discrete molecules separated by normal van der Waals distances. The P–P coupled eight-membered rings of the molecule are in *cis* position. This is remarkable as the structure of the related bi(cyclotriphosphazene) C₂H₆Cl₃N₆P₆ (Whittle, Desorcie & Allcock, 1985) adopts the *trans* conformation. The same *trans* conformation is reported for the phenyl derivatives (N₃P₃Cl₄Ph)₂ (Zoer & Wagner, 1972) and (N₃P₃Ph₄Me)₂ (Ahmed, 1976). Both eight-membered rings are significantly puckered with puckering amplitudes (Cremer & Pople, 1975) of 0.88 and 0.59 Å and average torsion angles of 39 and 38° for

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51262 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°)

Cl(11)—P(12)	2.001 (2)	P(12)—N(11)	1.558 (4)
Cl(12)—P(12)	2.003 (2)	P(12)—N(12)	1.559 (5)
Cl(13)—P(13)	1.998 (2)	P(13)—N(12)	1.558 (4)
Cl(14)—P(13)	2.002 (2)	P(13)—N(13)	1.574 (4)
Cl(15)—P(14)	1.998 (2)	P(14)—N(13)	1.567 (4)
Cl(16)—P(14)	2.009 (2)	P(14)—N(14)	1.551 (4)
Cl(21)—P(22)	2.009 (2)	P(21)—N(21)	1.595 (4)
Cl(22)—P(22)	2.005 (2)	P(21)—N(24)	1.589 (4)
Cl(23)—P(23)	1.992 (2)	P(21)—C(21)	1.776 (5)
Cl(24)—P(23)	2.010 (2)	P(22)—N(21)	1.551 (4)
Cl(25)—P(24)	1.994 (2)	P(22)—N(22)	1.557 (5)
Cl(26)—P(24)	1.997 (2)	P(23)—N(22)	1.562 (4)
P(11)—P(21)	2.194 (2)	P(23)—N(23)	1.558 (5)
P(11)—N(11)	1.597 (4)	P(24)—N(23)	1.553 (6)
P(11)—N(14)	1.588 (4)	P(24)—N(24)	1.537 (5)
P(11)—C(11)	1.785 (5)		
P(21)—P(11)—N(11)	110.8 (1)	N(21)—P(21)—C(21)	108.0 (2)
P(21)—P(11)—N(14)	98.9 (1)	N(24)—P(21)—C(21)	108.2 (2)
P(21)—P(11)—C(11)	106.8 (2)	Cl(21)—P(22)—Cl(22)	101.15 (7)
N(11)—P(11)—N(14)	119.6 (2)	Cl(21)—P(22)—N(21)	105.6 (2)
N(11)—P(11)—C(11)	106.9 (2)	Cl(21)—P(22)—N(22)	109.3 (2)
N(14)—P(11)—C(11)	113.0 (2)	Cl(22)—P(22)—N(21)	111.3 (2)
Cl(11)—P(12)—Cl(12)	101.63 (7)	Cl(22)—P(22)—N(22)	105.3 (2)
Cl(11)—P(12)—N(11)	110.5 (2)	N(21)—P(22)—N(22)	122.2 (2)
Cl(11)—P(12)—N(12)	105.5 (2)	Cl(23)—P(23)—Cl(24)	102.75 (9)
Cl(12)—P(12)—N(11)	106.0 (2)	Cl(23)—P(23)—N(22)	106.3 (2)
Cl(12)—P(12)—N(12)	109.3 (2)	Cl(23)—P(23)—N(23)	107.1 (2)
N(11)—P(12)—N(12)	122.0 (2)	Cl(24)—P(23)—N(22)	110.7 (2)
Cl(13)—P(13)—Cl(14)	102.87 (8)	Cl(24)—P(23)—N(23)	105.8 (3)
Cl(13)—P(13)—N(12)	105.5 (2)	N(22)—P(23)—N(23)	122.5 (3)
Cl(13)—P(13)—N(13)	109.4 (2)	Cl(25)—P(24)—Cl(26)	100.32 (9)
Cl(14)—P(13)—N(12)	110.3 (2)	Cl(25)—P(24)—N(23)	104.1 (2)
Cl(14)—P(13)—N(13)	105.2 (1)	Cl(25)—P(24)—N(24)	107.3 (2)
N(12)—P(13)—N(13)	122.0 (2)	Cl(26)—P(24)—N(23)	108.4 (3)
Cl(15)—P(14)—Cl(16)	101.62 (7)	Cl(26)—P(24)—N(24)	111.1 (2)
Cl(15)—P(14)—N(13)	109.7 (2)	N(23)—P(24)—N(24)	122.9 (3)
Cl(15)—P(14)—N(14)	105.9 (2)	P(11)—N(11)—P(12)	133.3 (3)
Cl(16)—P(14)—N(13)	104.4 (2)	P(12)—N(12)—P(13)	142.2 (3)
Cl(16)—P(14)—N(14)	111.6 (2)	P(13)—N(13)—P(14)	131.1 (2)
N(13)—P(14)—N(14)	121.9 (2)	P(11)—N(14)—P(14)	139.2 (3)
P(11)—P(21)—N(21)	106.4 (1)	P(21)—N(21)—P(22)	138.1 (3)
P(11)—P(21)—N(24)	106.5 (1)	P(22)—N(22)—P(23)	136.0 (3)
P(11)—P(21)—C(21)	107.4 (2)	P(23)—N(23)—P(24)	137.9 (4)
N(21)—P(21)—N(24)	119.8 (2)	P(21)—N(24)—P(24)	145.7 (3)

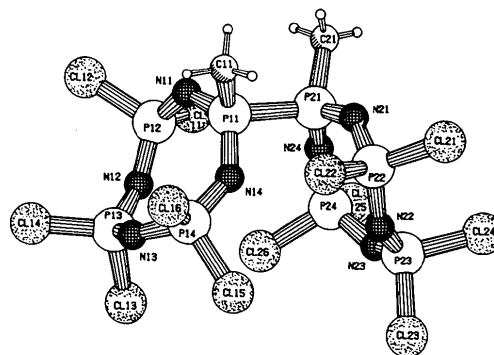


Fig. 1. Molecular structure with adopted numbering scheme.

1.550 (2) Å]. In accordance with this the P—N bonds in the P(Cl₂)—N—P(Cl₂) segments exhibit an intermediate value [mean 1.562 (2) Å].

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References

- AHMED, F. R. (1976). *Acta Cryst.* B32, 3078–3083.
 BOER, J. L. DE & DUSENBERG, A. J. M. (1984). *Acta Cryst.* A40, C410.
 CREMER, D. & POPE, J. A. (1975). *J. Am. Chem. Soc.* 97, 1354–1358.
 CROMER, D. T. & LIBERMAN, D. J. (1970). *J. Chem. Phys.* 53, 1891–1898.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
 DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* B31, 221–234.
 McCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* A31, 245–249.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure refinement. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1984). *SHELXS84*. Program for crystal structure determination. Univ. of Göttingen, Federal Republic of Germany.
 SPEK, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* A39, 158–166.
 WHITTLE, R. R., DESORCIE, J. L. & ALLCOCK, H. R. (1985). *Acta Cryst.* C41, 546–548.
 WINTER, H. (1986). Thesis. Univ. of Groningen, The Netherlands.
 WINTER, H. & VAN DE GRAMPPEL, J. C. (1984). *Recl Trav. Chim. Pays-Bas*, 103, 241–242.
 ZOER, H. & WAGNER, A. J. (1972). *Cryst. Struct. Commun.* 1, 17–21.

rings 1 and 2, respectively. The P atoms in ring 1 are approximately coplanar with the N atoms alternating above and below this plane resulting in approximate 4 symmetry in ring 1. Ring 2 is puckered irregularly. The P—P bond length 2.194 (2) Å is slightly shorter than the range 2.200–2.210 Å for the above-mentioned bi(cyclophosphazenes). In the P(Me)—N—P(Cl₂) segments the P—N bonds near the bridging P atoms are considerably longer than the other P—N bonds, which can be ascribed to the influence of the less electro-negative Me substituents on the π bonding in the ring [mean* values P(Me)—N 1.592 (2) and P(Cl₂)—N

* Throughout this paper the mean values and their standard deviations have been calculated according to Domenicano, Vaciego & Coulson (1975).