O(1), O(2) und O(3) eines Pyroanions koordiniert, Ag(2) verknüpft vier verschiedene Disilicatanionen über die terminalen O(3), O(1), O(3) und O(2), Ag(3) schliesslich verbrückt beide O(1) einer $Si_2O_7^{6-}$-Gruppe mit O(2) und O(4) zweier weiterer Anionen. Wie schon bei anderen silberreichen Oxiden (vgl. Keller & Müller-Buschbaum, 1973; Jansen, 1975) treten auch in $Ag_6Si_2O_7$ mit 2,95 Å vergleichsweise kurze Ag–Ag Abstände auf (im metallischen Silber ist $d_{Ag–Ag} = 2,89$ Å).

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1,3-Di-*tert*-butyl-2,4-bis(dimethylamino)-2,4-dithio-*cyclo*-di(phosphazane)

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Abstract. $C_{12}H_{30}N_4P_2S_2$, $M_r = 356\cdot5$. (i) *cis*-Isomer, m.p. 214°C, monoclinic, $P2_1/c$, $a = 9\cdot255$, $b = 15\cdot215$, $c = 14\cdot927$ Å, $\beta = 109\cdot33°$, $V = 1983$ Å³, $Z = 4$, $D_c = 1\cdot194$ g cm⁻³; Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 4\cdot1$ cm⁻¹. (ii) *trans*-Isomer, m.p. 256°C, orthorhombic, *Pbca*, $a = 12\cdot50$, $b = 12\cdot35$, $c = 12\cdot62$ Å, $V = 1948$ Å³, $Z = 4$, $D_c = 1\cdot215$ g cm⁻³, molecular symmetry C_i; Cu $K\alpha$, $\lambda = 1\cdot5418$ Å. The structure of the *cis*-isomer has been determined from 2728 diffractometric intensity data refined to $R = 0\cdot042$. The phosphazane ring is non-planar, as is the coordination of the endocyclic N atoms, whereas the dimethylamino PNC_2 units are flat.

Introduction. Geometric isomers of $[Me_2NP(S)NBu^t]_2$ have recently been isolated by Keat & Thompson (1977). Clearcut assignment of a *cis* or *trans* configuration to each isomer proved difficult on the basis of spectroscopic experiments. Accordingly, diffraction studies were initiated.

The space groups and cell dimensions of both isomers were first determined from oscillation and Weissenberg photographs. In the orthorhombic isomer crystallographic C_i symmetry is imposed on each molecule. Since this is consistent only with a *trans* configuration no further experiments were undertaken with the orthorhombic isomer.

No symmetry is imposed on the molecules in the monoclinic modification and a complete structure analysis was therefore carried out. Full descriptions of the techniques used have been given elsewhere (Manojlović-Muir & Muir, 1974). Accurate cell dimensions and the intensities of all independent reflexions with $\theta \le 26°$ were measured on a Hilger & Watts Y290 diffractometer, equipped with a graphite monochromator, using Mo radiation. Intensity measurements were made with a symmetrical θ–2θ scan of 30 0·02° steps in θ. Counting continued for 2 s at each step. Stationary crystal–stationary counter backgrounds were measured for 15 s at each end of the scan. The intensities of three standard reflexions, periodically remeasured during the experiment, varied by less than ±4% of their mean values. The intensities and their standard deviations ($q = 0\cdot06$) were corrected for Lorentz and polarization factors. 2728 reflexions with $I \ge 3\sigma(I)$ were used in the subsequent analysis.

The positions of the S and P atoms were obtained

Table 1. *Fractional atomic coordinates* ($\times 10^4$)

	x	y	z
S(1)	305 (1)	1909 (1)	2606 (1)
S(2)	4967 (1)	3060 (1)	2947 (1)
P(1)	805 (1)	2352 (1)	1533 (1)
P(2)	3391 (1)	2981 (1)	1719 (1)
N(1)	2450 (3)	2020 (2)	1377 (2)
N(2)	1614 (3)	3356 (1)	1605 (2)
N(3)	−657 (3)	2256 (2)	563 (2)
N(4)	3983 (3)	3368 (2)	878 (2)
C(1)	3071 (4)	1109 (2)	1394 (3)
C(2)	4359 (6)	1143 (3)	967 (4)
C(3)	3682 (6)	764 (3)	2398 (4)
C(4)	1763 (6)	540 (3)	795 (4)
C(5)	1138 (4)	4210 (2)	1919 (2)
C(6)	1920 (5)	4944 (2)	1571 (3)
C(7)	−586 (5)	4294 (3)	1472 (4)
C(8)	1558 (6)	4250 (3)	2993 (3)
C(9)	−2080 (4)	1819 (3)	508 (3)
C(10)	−645 (5)	2560 (4)	−365 (3)
C(11)	3017 (6)	3349 (4)	−130 (3)
C(12)	5437 (5)	3792 (4)	1007 (4)

from the three-dimensional Patterson function and those of the remaining atoms from subsequent difference syntheses. Refinement was by blocked-matrix least-squares minimization of the function $\Sigma [(|F_o| - |F_c|)/\sigma(F_o)]^2$. The H scattering factor of Stewart, Davidson & Simpson (1965) was used. Scattering factors and dispersion corrections for other atoms were taken from *International Tables for X-ray Crystallography* (1974).

Adjustment of the positional and anisotropic thermal parameters of the non-hydrogen atoms gave $R = 0.077$ and $R_w = 0.123$. After refinement of the positions and isotropic temperature factors of the H atoms as well (301 parameters in all) R was 0.042 and R_w 0.073. During the final cycles of refinement three strong, low-angle reflexions, apparently suffering from extinction, were excluded from the least-squares calculations. The final difference synthesis displayed only random fluctuations of electron density between +0.3 and −0.4 e Å^{-3}. The relative constancy of mean $w\Delta^2$ values when analysed as a function of $\sin \theta$ and of $|F_o|$ indicated that a satisfactory weighting scheme had been used.

The final parameters of the non-hydrogen atoms and some functions derived from them are presented in Tables 1–4. A view of the molecule is shown in Fig. 1. Since the H atom positions have been established with only moderate accuracy bond lengths and angles involving them will not be discussed here.*

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* Lists of structure factors, anisotropic thermal parameters, final hydrogen atom parameters, bond lengths and angles involving hydrogen atoms and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32851 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Calculations were performed with the XRAY 72 system (Stewart, 1972) and the *GEOM* program of Dr P. Mallinson on the NUMAC IBM 370 computer.

Discussion. The monoclinic crystals contain well-separated [Me$_2$NP(S)NBu^t]$_2$ molecules of *cis*-configuration. Chemically equivalent bond lengths and valency angles agree well (Tables 2 and 3) and the mean values shown in Fig. 2 will therefore be used in the subsequent discussion. Three intermolecular contacts involving the heavier atoms are shorter than the sums of the corresponding van der Waals radii: S(1)$\cdots$C(10^i) 3.52, S(1)$\cdots$C(11^i) 3.50 and C(7)$\cdots$C(12^{ii}) 3.60 Å [(i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x - 1, y, z$].

The conformations about the exocyclic P—N and N—C bonds are such that the overall symmetry of the molecule is close to C_{2v}. One non-crystallographic mirror plane is defined by the atoms N(1), N(2), C(1), C(3), C(5) and C(8) which are coplanar to ± 0.02 Å (Table 4 plane *b*). A second, at right angles to the first, is defined by the atoms S(1), S(2), P(1), P(2), N(3), N(4) and C(9)—C(12) which deviate from coplanarity by up to 0.08 Å (Table 4 plane *c*). This, the most serious distortion from C_{2v} symmetry, arises

Table 2. *Bond lengths* (Å)

S(1)–P(1)	1.929 (1)	N(3)–C(9)	1.453 (5)
S(2)–P(2)	1.932 (1)	N(3)–C(10)	1.463 (6)
P(1)–N(1)	1.692 (3)	N(4)–C(11)	1.474 (5)
P(1)–N(2)	1.689 (2)	N(4)–C(12)	1.447 (6)
P(1)–N(3)	1.629 (2)	C(1)–C(2)	1.528 (8)
P(2)–N(1)	1.692 (2)	C(1)–C(3)	1.509 (6)
P(2)–N(2)	1.696 (3)	C(1)–C(4)	1.517 (6)
P(2)–N(4)	1.636 (4)	C(5)–C(6)	1.514 (6)
N(1)–C(1)	1.498 (4)	C(5)–C(7)	1.518 (5)
N(2)–C(5)	1.497 (4)	C(5)–C(8)	1.520 (6)

Table 3. *Interbond angles* (°)

N(1)–P(1)–S(1)	118.97 (10)	N(2)–P(1)–S(1)	119.14 (9)
N(3)–P(1)–S(1)	110.48 (11)	N(1)–P(2)–S(2)	119.43 (10)
N(2)–P(2)–S(2)	118.51 (9)	N(4)–P(2)–S(2)	111.52 (13)
N(2)–P(1)–N(1)	83.00 (12)	N(3)–P(1)–N(1)	111.77 (14)
P(2)–N(1)–P(1)	95.60 (12)	C(1)–N(1)–P(1)	129.16 (23)
N(3)–P(1)–N(2)	110.95 (14)	P(2)–N(2)–P(1)	95.59 (12)
C(5)–N(2)–P(1)	129.41 (22)	C(9)–N(3)–P(1)	124.16 (25)
C(10)–N(3)–P(1)	123.30 (28)	N(2)–P(2)–N(1)	82.80 (12)
N(4)–P(2)–N(1)	110.40 (15)	C(1)–N(1)–P(2)	129.66 (24)
N(4)–P(2)–N(2)	111.21 (14)	C(5)–N(2)–P(2)	129.55 (21)
C(11)–N(4)–P(2)	122.17 (31)	C(12)–N(4)–P(2)	126.23 (30)
C(2)–C(1)–N(1)	108.02 (31)	C(3)–C(1)–N(1)	110.79 (32)
C(4)–C(1)–N(1)	106.92 (33)	C(6)–C(5)–N(2)	108.00 (29)
C(7)–C(5)–N(2)	108.10 (28)	C(8)–C(5)–N(2)	111.49 (28)
C(10)–N(3)–C(9)	112.46 (32)	C(12)–N(4)–C(11)	111.55 (37)
C(3)–C(1)–C(2)	109.80 (40)	C(4)–C(1)–C(2)	110.71 (38)
C(4)–C(1)–C(3)	110.53 (36)	C(7)–C(5)–C(6)	109.82 (32)
C(8)–C(5)–C(6)	110.40 (33)	C(8)–C(5)–C(7)	108.99 (36)

mainly from twisting of the dimethylamino groups about the P—N bonds by ca 4° and appears to be a consequence of intramolecular overcrowding. Despite the distortion, the methyl C atoms C(10) and C(11) are separated by only 3·50 Å and the S(1)···C(9) and S(2)···C(12) contacts, respectively 3·18 and 3·26 Å, are also short.

Relief of overcrowding may also explain the non-planarity of the $(P-N)_2$ ring in cis-[Me₂NP(S)NBuᵗ]₂. The internal torsion angle about the P—N ring bond is 13°, rather larger than the corresponding value of 8° in cis-[PhP(S)NEt]₂, the only other structurally

characterized cyclo-di(phosphazane) of cis-configuration (Ibrahim et al., 1971; Bullen & Tucker, 1973). By contrast, all trans-cyclo-di(phosphazane) molecules so far studied have been found to be constrained to C_i symmetry in the solid, so that the $(P-N)_2$ rings are exactly planar {e.g. trans-[PhP(S)NEt]₂ (Bullen, Rutherford & Tucker, 1973), trans-[PhP(S)NPh]₂ (Peterson & Wagner, 1973), trans-[PhP(S)NMe]₂ (Cameron, Howlett & Prout, 1975), trans-[C₁₅H₁₅N₂PS]₂ (Cameron, Howlett & Prout, 1977), trans-[ClP(O)NBuᵗ]₂ (Manojlović-Muir & Muir, 1974)}.

The bond lengths and valency angles in the $(P-N)_2$ ring of cis-[Me₂NP(S)NBuᵗ]₂ agree excellently with corresponding values not only in cis-[PhP(S)NEt]₂ but also in trans-cyclo-di(phosphazanes), with the exception of trans-[C₁₅H₁₅N₂PS]₂ (Cameron et al., 1975) where unusually long ring P—N distances of 1·74 (2) and 1·80 (2) Å are found. The P—S bond lengths of 1·930 (2) Å found here are also typical of the values in dithio-cyclo-di(phosphazanes) and are consistent with a substantial degree of multiple character.

In contrast to our earlier suggestion (Manojlović-Muir & Muir, 1974) the valency angles at the P atoms do not follow the rule that the widest angle is formed by the bonds of highest order. The S—P—N(ring) angles are some 8° more obtuse than the S—P—N-(amino) angles, yet the exocyclic P—N bonds are 0·06 Å shorter than those in the $(P-N)_2$ ring; their average length of 1·633 (4) Å is similar to the value of 1·641 (2) Å in Ph₂FP=NMe (Adamson & Bart, 1970) where substantial donation of the N lone pairs to P seems likely. The greater length of the ring P—N bonds in cis-[Me₂NP(S)NBuᵗ]₂ is perhaps to be expected, since the lone pairs of the ring N atoms are shared by two P atoms whereas those of the amino N atoms interact with only one P. Apart from the rather short exocyclic P—N bonds the geometries of the dimethylamino groups appear similar to those found,

Table 4. *Deviations of atoms from least-squares planes* (Å ×10³)

The coordinates X,Y,Z are referred to an orthonormal basis set defined by a, b and c*.

(a) $-0.039X - 0.172Y + 0.984Z = 1.498$

P(1)	14	P(2)	17
N(1)	−179	N(2)	−177
C(1)	62	C(5)	60

(b) $0.919X + 0.383Y + 0.089Z = 2.803$

N(1)	7	N(2)	−1
C(1)	−2	C(5)	−11
C(3)	−14	C(8)	16

(c) $0.397X - 0.908Y - 0.139Z = 3.548$

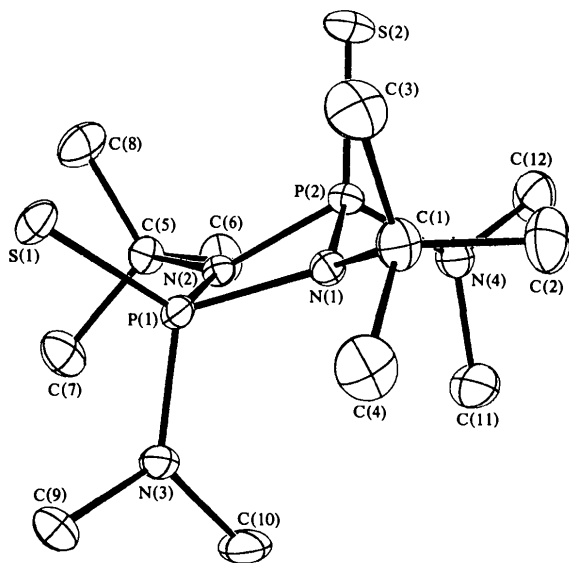| P(1)	−4	P(2)	6
S(1)	3	S(2)	−5
N(3)	−28	N(4)	19
C(9)	74	C(11)	85
C(10)	−79	C(12)	−83

Fig. 1. A perspective view of the molecule. 50% probability ellipsoids are displayed. H atoms are omitted for clarity.
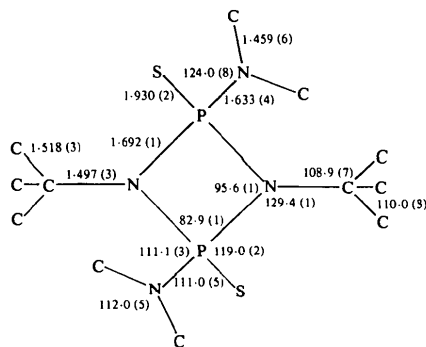

Fig. 2. Mean bond lengths (Å) and interbond angles (°). The standard deviations of the means are the larger of the estimates (i) $(\Sigma\, \sigma_i^{-2})^{-1/2}$ and (ii) $\{\Sigma[(x_i - \bar{x})/\sigma_i]^2/(n - 1)\,\Sigma\,\sigma_i^{-2}\}^{1/2}$; the summations are over n individual observations x_i with standard deviations σ_i.

for example, in large-ring *cyclo*-poly(phosphazenes) such as $N_6P_6(NMe_2)_{12}$ (Wagner & Vos, 1968). The PNC_2 units are coplanar to within ±0·02 Å.

In contrast, the coordination of the phosphazane-ring N atoms N(1) and N(2) is appreciably pyramidal, each N atom lying 0·21 Å from the plane defined by adjacent P and C atoms. Despite the statement of Peterson & Wagner (1973), which has been widely accepted by other authors (*e.g.* Cameron *et al.*, 1977), planar coordination appears to be the exception rather than the rule for phosphazane N atoms: thus in *cis*- and *trans*-[PhP(S)NEt]₂ the N atoms are displaced by up to 0·24 Å from the P_2C planes (Bullen & Tucker, 1973; Bullen, Rutherford & Tucker, 1973) and values of 0·14 and 0·28 Å are reported for similar displacements in *trans*-[PhP(S)NMe]₂ (Cameron *et al.*, 1975) and *trans*-[ClP(O)NBuᵗ]₂ (Manojlović-Muir & Muir, 1974); only in *trans*-[PhP(S)NPh]₂ (Peterson & Wagner, 1973) does an accurately planar phosphazane-N environment occur. It should be noted that these variations in the degree of planarity of the bonds from phosphazane N atoms are achieved with relatively minor alterations in valency angles. Corresponding angles at N in *trans*-[PhP(S)NPh]₂ disagree by no more than 2·5° with those found here. It is also worth emphasizing that the sum of the valency angles at N is a poor test of the coplanarity of the valencies. The sums of angles at N(1), and N(2), respectively 354 and 355°, do not differ substantially from 360°. To summarize, the available results on *cyclo*-di(phosphazanes) indicate that a range of N coordinations can occur with little change in bond lengths or valency angles. This view conflicts with that of Cameron, Howlett & Prout (1977), who attempt to explain unusually long P—N ring distances in [$C_{15}H_{15}N_2PS$]₂ in terms of the non-planarity of the bonds to the ring N atoms.

The N—CMe₃ distance of 1·497 (3) Å found here

agrees with the corresponding distance of 1·507 (5) Å in *trans*-[ClP(O)NBuᵗ]₂ (Manojlović-Muir & Muir, 1974). It appears to be significantly longer than the N—CH₃ and N—Et distances in [PhP(S)N*R*]₂, *R* = Me, Et, all of which are close to 1·46 Å.

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α-Tetrakis(4-methylpyridine)diisothiocyanatonickel(II)

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Abstract. $C_{26}H_{28}N_6S_2Ni$, $M_r = 547·4$, monoclinic, $P2_1/c$, $a = 19·205$ (1), $b = 9·768$ (1), $c = 16·765$ (1) Å, $\beta = 113·544$ (3)°, $U = 2883$ Å³, $Z = 4$, $D_x = 1·261$ g cm⁻³, $F(000) = 1144$, μ(Cu $K\alpha$, $\lambda = 1·5418$ Å) = 25·7 cm⁻¹. The structure was refined to $R = 0·042$. It consists of discrete propeller-shaped molecules, with the pitch of the four pyridine blades ranging from 49 to 60°. Ni is octahedrally coordinated to the N atoms of