Molecular geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

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Structures of Spirocyclic Phosphathiazenes: $(Ph_6P_3N_4)S(S_2N_3)$

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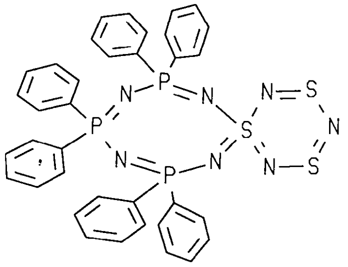
Abstract. 3,5,7-Triphenyl-1λ^6,2,4,6,8,3λ^5,5λ^5,7λ^5-thiatetraazatriphosphocine-1-spiro-1′-1′λ^6,2′,4′,6′-thiatriazadiphosphorine, $C_{36}H_{30}N_7P_3S_3$, $M_r = 749{\cdot}8$, triclinic, $P\bar{1}$, $a = 9{\cdot}547\ (2)$, $b = 12{\cdot}554\ (3)$, $c = 15{\cdot}330\ (3)$ Å, $\alpha = 92{\cdot}01\ (2)$, $\beta = 102{\cdot}77\ (2)$, $\gamma = 92{\cdot}31\ (2)°$, $V = 1789\ (1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}39$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 3{\cdot}7$ cm^{-1}, $F(000) = 776$, $T = 293$ K, $R = 0{\cdot}069$ for 2881 unique observed reflections. The molecule is composed of a six-membered S_3N_3 ring and an eight-membered $(PPh_2)_3SN_4$ ring joined by an S atom which is common to both rings. In the S_3N_3 ring one of the N atoms (N5) adjacent to the unique S atom is 0·746 (7) Å out of the plane of the rest of the S_3N_2 unit, which is planar within 0·05 Å. The P_3SN_4 ring adopts a distorted tub configuration with the tub 'end' atoms (P1,N2,P3,N4) displaced 0·79–1·08 Å from the other four atoms which are planar within 0·05 Å.

Experimental. Crystals of (I) obtained from acetonitrile solutions. Dark-blue platelet data crystal 0·14 × 0·38 × 0·42 mm mounted on glass fiber. Intensities measured with an Enraf–Nonius CAD-4 diffractometer using ω–2θ scans of 4 to 16° min^{-1} in θ. Unit cell determined from least-squares analysis of angle data for 25 reflections with $16 < 2\theta < 19°$. Analytical absorption correction based on crystal shape varied from 0·90 to 1·00. Data collected to $(\sin\theta)/\lambda$ of 0·60 Å^{-1}, $-11 < h < 11$, $-14 < k < 14$, $-18 < l < 0$. Four standard reflections ($\bar{1}\bar{1}\bar{6}$, $23\bar{5}$, $\bar{3}3\bar{1}$, $3\bar{3}0$) decreased less than 0·9% over 50·9 h of data collection. 6533 reflections measured, 6277 unique ($R_{int} = 0{\cdot}02$), 2657 reflections with $I < 3\sigma(I)$ considered unobserved.



(I)

Solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). Full-matrix least squares minimized $\sum w(\Delta F)^2$. H atoms were constrained to idealized positions (C—H = 0·95 Å) with isotropic thermal parameters, $B = 12{\cdot}0$ Å^2. One phenyl group (C31) showed a rotational disorder which was best modeled by four isotropic half-occupancy C atom positions along with the P-bonded C atom and the *trans* C—H group; all other non-H atoms refined anisotropically for a total of 438 variables. The C25 phenyl ring has very high thermal parameters indicating extensive thermal motion and/or disorder; high thermal parameters rather than our attempts at disorder models gave the best refinement. $R = 0{\cdot}069$, $wR = 0{\cdot}088$, $S = 2{\cdot}21$, where non-Poisson $w^{-1} = [\sigma^2(I) + 0{\cdot}0025I^2]/4F^2$. Final $(\Delta/\sigma)_{max} < 0{\cdot}5$, $\Delta\rho_{max} = 0{\cdot}55\ (3)$

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Table 1. *Fractional coordinates and isotropic or equivalent isotropic thermal parameters*

The thermal parameters are of the form $B = 8\pi^2U$ and

$$B_{eq} = \tfrac{8}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

Starred atoms were refined isotropically.

	x	y	z	B/B_{eq}(Å^2)
S1	0·7763 (3)	0·0794 (2)	0·7175 (1)	4·68 (5)
S2	0·7394 (3)	−0·1015 (2)	0·6112 (2)	7·49 (7)
S3	0·9765 (3)	0·0352 (2)	0·6142 (2)	6·96 (7)
P1	0·6494 (2)	0·2437 (2)	0·6124 (1)	3·51 (4)
P2	0·7708 (3)	0·3825 (2)	0·7652 (1)	4·01 (5)
P3	0·7284 (3)	0·1960 (2)	0·8662 (1)	6·33 (6)
N1	0·7480 (6)	0·3398 (5)	0·6637 (4)	3·9 (1)
N2	0·6438 (7)	0·1332 (5)	0·6618 (4)	4·2 (2)
N3	0·8175 (8)	0·1138 (5)	0·8168 (4)	6·1 (2)
N4	0·7089 (9)	0·3132 (5)	0·8326 (4)	6·2 (2)
N5	0·7570 (9)	−0·0467 (5)	0·7133 (5)	6·9 (2)
N6	0·8843 (8)	−0·0652 (7)	0·5751 (5)	7·1 (2)
N7	0·9177 (7)	0·1129 (5)	0·6788 (4)	4·7 (2)
C1	0·7001 (7)	0·2160 (6)	0·5085 (5)	3·8 (2)
C2	0·6412 (9)	0·1281 (7)	0·4557 (5)	5·0 (2)
C3	0·671 (1)	0·1030 (7)	0·3763 (6)	6·8 (3)
C4	0·764 (1)	0·1686 (8)	0·3469 (6)	7·4 (3)
C5	0·830 (1)	0·2597 (9)	0·3959 (6)	7·5 (3)
C6	0·7943 (9)	0·2834 (8)	0·4783 (5)	5·4 (2)
C7	0·4652 (8)	0·2781 (6)	0·5809 (5)	5·0 (2)
C8	0·357 (1)	0·2344 (8)	0·6144 (7)	8·6 (3)
C9	0·213 (1)	0·2752 (9)	0·5886 (8)	10·6 (3)
C10	0·196 (1)	0·357 (1)	0·533 (1)	12·6 (5)
C11	0·294 (1)	0·396 (1)	0·500 (1)	12·1 (5)
C12	0·4304 (9)	0·3574 (8)	0·5229 (8)	8·0 (3)
C13	0·551 (1)	0·1371 (7)	0·8662 (5)	7·6 (3)
C14	0·534 (1)	0·0299 (8)	0·8796 (6)	8·4 (3)
C15	0·402 (1)	−0·016 (1)	0·8791 (7)	10·4 (4)
C16	0·290 (1)	0·044 (1)	0·8692 (8)	13·9 (4)
C17	0·292 (1)	0·146 (1)	0·854 (1)	14·9 (5)
C18	0·426 (1)	0·1965 (9)	0·8525 (9)	12·4 (4)
C19	0·831 (1)	0·2011 (6)	0·9788 (5)	6·8 (3)
C20	0·947 (1)	0·1401 (7)	1·0080 (6)	7·3 (3)
C21	1·019 (1)	0·1445 (8)	1·0966 (6)	9·1 (4)
C22	0·977 (2)	0·2133 (9)	1·1565 (6)	11·1 (4)
C23	0·864 (2)	0·2753 (8)	1·1293 (6)	12·6 (4)
C24	0·790 (1)	0·2693 (8)	1·0453 (6)	10·6 (3)
C25	0·9630 (9)	0·4100 (6)	0·8021 (6)	6·9 (2)
C26	1·025 (1)	0·4098 (9)	0·8938 (8)	13·0 (4)
C27	1·181 (2)	0·432 (1)	0·918 (1)	21·5 (5)
C28	1·246 (1)	0·455 (1)	0·856 (1)	22·9 (6)
C29	1·189 (1)	0·459 (1)	0·763 (1)	16·9 (5)
C30	1·046 (1)	0·432 (1)	0·7402 (9)	11·5 (4)
C31	0·6893 (8)	0·5106 (6)	0·7699 (5)	4·0 (2)
C32	0·617 (2)	0·562 (2)	0·701 (1)	6·3 (4)*
C33	0·574 (2)	0·672 (2)	0·709 (1)	8·2 (6)*
C34	0·562 (1)	0·7060 (8)	0·7788 (7)	7·2 (3)
C35	0·639 (3)	0·672 (2)	0·857 (2)	10·9 (8)*
C36	0·670 (3)	0·553 (2)	0·854 (2)	9·8 (7)*
C42	0·774 (2)	0·602 (2)	0·790 (1)	7·3 (5)*
C43	0·698 (3)	0·704 (2)	0·784 (2)	9·6 (7)*
C45	0·483 (3)	0·614 (2)	0·733 (2)	8·9 (6)*
C46	0·547 (3)	0·500 (2)	0·744 (2)	9·2 (6)*

and $\Delta\rho_{min} = -0{\cdot}29$ (3) e Å^{-3} on final difference map. Atomic scattering factors and anomalous-dispersion correction from *International Tables for X-ray Crystallography* (1974) and programs used were those of Enraf–Nonius (1982) *SDP*.* Table 1 gives the atom coordinates and Fig. 1 shows the ring atoms with the numbering scheme, and Table 2 gives the distances and angles involving the ring atoms.

Table 2. *Selected bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

S1–N2	1·555 (5)	P1–C1	1·792 (6)
S1–N3	1·528 (5)	P1–C7	1·792 (7)
S1–N5	1·584 (5)	P2–N1	1·593 (4)
S1–N7	1·636 (5)	P2–N4	1·570 (5)
S2–N5	1·659 (5)	P2–C25	1·812 (7)
S2–N6	1·653 (6)	P2–C31	1·821 (5)
S3–N6	1·531 (6)	P3–N3	1·631 (5)
S3–N7	1·572 (5)	P3–N4	1·580 (5)
P1–N1	1·573 (4)	P3–C13	1·824 (9)
P1–N2	1·607 (5)	P3–C19	1·785 (7)
N2–S1–N3	115·4 (3)	N4–P2–C25	112·1 (4)
N2–S1–N5	112·8 (3)	N4–P2–C34	104·7 (3)
N2–S1–N7	108·7 (2)	C25–P2–C34	105·9 (3)
N3–S1–N5	106·1 (3)	N3–P3–N4	119·2 (3)
N3–S1–N7	104·8 (3)	N3–P3–C13	110·3 (3)
N5–S1–N7	108·6 (3)	N3–P3–C19	101·8 (3)
N5–S2–N6	107·6 (3)	N4–P3–C13	107·8 (4)
N6–S3–N7	118·3 (3)	N4–P3–C19	109·5 (3)
N1–P1–N2	118·8 (2)	C13–P3–C19	107·6 (4)
N1–P1–C1	108·7 (3)	P1–N1–P2	129·7 (3)
N1–P1–C7	111·4 (3)	S1–N2–P1	125·3 (3)
N2–P1–C1	108·0 (3)	S1–N3–P3	124·6 (4)
N2–P1–C7	104·4 (3)	P2–N4–P3	135·4 (4)
C1–P1–C7	104·7 (3)	S1–N5–S2	113·6 (3)
N1–P2–N4	119·0 (2)	S2–N6–S3	121·3 (3)
N1–P2–C25	104·7 (3)	S1–N7–S3	121·5 (3)
N1–P2–C31	109·8 (3)		

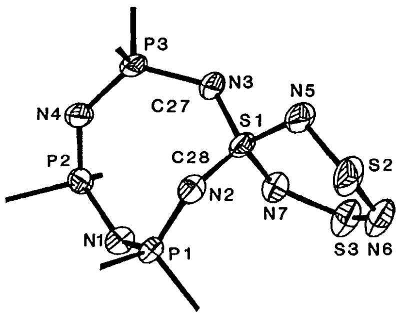

Fig. 1. *ORTEP*II diagram (Johnson, 1976) for the ring atoms (phenyl rings omitted for figure clarity).

Related literature. The spirocyclic nature of the structure is to be compared with that of $(Ph_4P_2N_3)_2S$ (Chivers, Rao & Richardson, 1985) and $(Ph_6P_3N_4)_2S$ (Oakley & Cordes, 1988). The structural parameters and non-planarity of the six-membered S_3N_3 ring are similar to those seen in $PNP^+S_3N_3O_2^-$ (Chivers, Cordes, Oakley & Pennington, 1983) and $Ph_2PS_2N_3$ (Burford, Chivers, Cordes, Laidlaw, Noble, Oakley & Swepston, 1982). The tub-like conformation of the eight-membered ring is comparable to the conformations of sterically crowded eight-membered cyclophosphazenes (Paddock, 1964; Bullen & Tucker, 1972; Bullen & Dann, 1974).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51074 (45 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1988). C**44**, 1840–1842

Structures of Spirocyclic Phosphathiazenes: $(Ph_6P_3N_4)_2S$

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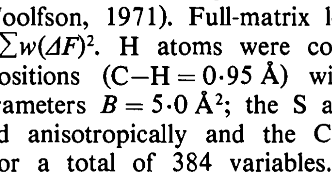
Abstract. 3,3′,5,5′,7,7′-Hexaphenylspirobi($1\lambda^6$,2,4,6,8,$3\lambda^5$,$5\lambda^5$,$7\lambda^5$-thiatetraazatriphosphocine), $C_{72}H_{60}N_8P_6S$, $M_r = 1255{\cdot}2$, orthorhombic, *Pbca*, $a = 49{\cdot}76\,(1)$, $b = 13{\cdot}104\,(6)$, $c = 19{\cdot}59\,(1)$ Å, $V = 12774\,(15)$ Å^3, $Z = 8$, $D_x = 1{\cdot}31$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 2{\cdot}7$ cm^{-1}, $F(000) = 5232$, $T = 293$ K, $R = 0{\cdot}068$ for 2704 unique observed reflections. Two SP_3N_4 rings share the S atom in the spiro molecule. One of the rings is roughly in the saddle (S_4N_4) conformation with the N atoms 0·55 (1) to 0·76 (1) Å above and below the S—P4—P5—P6 group which is planar within 0·130 (4) Å. The other ring is approximately in a tub conformation, with the S—N4 and P2—N2 tub ends displaced 0·68 to 1·09 Å from the P1—N1—P3—N3 boat bottom which is planar within 0·03 Å. The average S—N, N—P, P—N and N—P bond distances (moving out in the rings from the S atom) are 1·56 (2), 1·61 (2), 1·58 (2) and 1·58 (2) Å, respectively. The NSN, NPN, SNP and PNP bond angles average 109 (6), 121 (3), 127 (1) and 132 (3)°, respectively.

Experimental. Compound (I) prepared as a minor by-product of the reduction of $(PPh_2)_3N_4SCl$ with $SbPh_3$. The pale yellow crystal used for data collection was obtained from acetonitrile solution. Data crystal 0·2 × 0·4 × 0·5 mm mounted on a glass fiber. Intensities measured with an Enraf–Nonius CAD-4 diffractometer using ω–2θ scans of 4–16° min^{-1} in θ. Unit cell determined from least-squares analysis of angle data for 22 reflections with $18 < 2\theta < 22°$. No absorption correction was made. Data collected to $(\sin\theta)/\lambda$ of 0·47 Å^{-1}, $0 < h < 46$, $0 < k < 12$, $0 < l < 18$. Three standard reflections (383, 467, 5,1,12) decreased less than 0·5% over 46·3 h of data collection. 5361 reflections measured, 2657 reflections with $I < 3\sigma(I)$ considered unobserved.



(I)

Solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971). Full-matrix least squares minimized $\sum w(\Delta F)^2$. H atoms were constrained to idealized positions (C—H = 0·95 Å) with isotropic thermal parameters $B = 5{\cdot}0$ Å^2; the S and P atoms were refined anisotropically and the C atoms isotropically for a total of 384 variables. $R = 0{\cdot}068$, $wR = 0{\cdot}078$, $S = 1{\cdot}79$, where non-Poisson $w^{-1} = [\sigma^2(I) + 0{\cdot}0025I^2]/4F^2$. $R = 0{\cdot}11$ for all reflections with $F_{\text{obs}} > 0$ and 0·19 for all reflections (1773 had $F_{\text{obs}} = 0$). Final $(\Delta/\sigma)_{\max} < 0{\cdot}4$, $\Delta\rho_{\max} = 0{\cdot}46\,(4)$ and $\Delta\rho_{\min} =$

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