Crystal Structure of 2,2,4,4,6-Pentafluoro-6-[*N*-(1,2,4,3,5-trithiadiazol-1-ylidene)amino]cyclotriphosphazene, $S_3N_2NP_3N_3F_5$

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Crystals of the title compound are orthorhombic, space group *Pbca* with *a* = 15.915(3), *b* = 14.641(3), *c* = 6.700(3) Å, and *Z* = 8. The structure was solved from diffractometer data using direct methods and refined by least-squares to *R* = 0.037 for 1 528 observed reflections. The molecule consists of a cyclotriphosphazene ring bonded through a bridging nitrogen atom to a five-membered S_3N_2 ring.

THE number of substituted five-membered sulphur-nitrogen ring compounds is small.[1] So far only S_3N_2X derivatives are known and investigated by *X*-ray analyses, where X contains an electron-withdrawing group, *e.g.* Cl_2,[2] O,[3] NSO_2F,[4,5] or $NC(O)CF_3$.[6] All the compounds are sensitive to moisture and are readily decomposed in wet air. In contrast we observed that the title compound $S_3N_2NP_3N_3F_5$ is kinetically much more stable and can be kept in open air without decomposition. It was prepared [7] in high yield by the reaction of $P_3N_3F_5$-$N[Sn(CH_3)_3]_2$ and $S_3N_2Cl_2$. The present study was undertaken to examine the structure and the nature of bonding in the sulphur–nitrogen portion of the molecule to interpret the different properties of the five-membered rings.

EXPERIMENTAL

The crystals were obtained by sublimation as well formed yellow prisms, elongated along *c* and showing prominent [1 0 0] and [0 1 0] faces. The crystal used for data collection had dimensions 0.5 × 0.3 × 0.3 mm and was sealed in a thin-walled quartz capillary.

Crystal Data.—$F_5N_6P_3S_3$, $M = 368.13$, Orthorhombic, space group *Pbca*, $a = 15.915(3)$, $b = 14.641(3)$, $c = 6.700(3)$ Å, $U = 2\,260.2$ Å^3, $D_m = 2.09$, $Z = 8$, $D_c = 2.16$ g cm^{-3}, $F(000) = 2\,945.04$, $\mu = 11.1$ cm^{-1} for Mo-K_α radiation, $\lambda = 0.7107$ Å.

Intensity data were collected on a Hilger and Watts Y290 four-circle diffractometer using zirconium-filtered Mo-radiation employing a 2θ—ω scan. 1 993 Independent reflections were recorded in the range $0 < \theta < 25°$ of which 1 528 were taken as observed having net counts $> 2.5\sigma$. Intensities were corrected for Lorentz and polarisation effects but not for absorption. Unit-cell parameters were obtained by a least-squares treatment of the positions of 12 high-order reflections.[8]

Structure Determination and Refinement.—The structure was solved by direct methods using a multisolution program.[9] Phases were assigned to the 230 normalised structure factors having $E > 1.62$. An *E* map calculated from the most self-consistent set of phases (consistency index 0.84) revealed the correct positions of all atoms except F(2) and N(3). Refinement using the method of least squares with the block-diagonal approximation ($R = 0.26$) and the calculation of a difference-Fourier map gave the correct positions of F(2) and N(3). Further refinement with anisotropic thermal parameters for all atoms gave an *R* value of 0.045. The refinement was completed using full-matrix least-squares methods which saw *R* converge to its final value of 0.037 for the 1 528 observed reflections.

A difference-Fourier map calculated from the final structure factors showed no peaks with heights > 0.3 e Å^{-3}. The parameter shifts in the last cycle of refinement were all $< 0.3\sigma$. The weighting scheme used took the form [10] $\sqrt{w} = 2N/|F_o|[T + gB + (0.06\,N)^2]^{\frac{1}{2}}$ where *N* is the net count and *g* is the ratio of the time spent measuring the total count (*T*) to that spent measuring the two backgrounds whose sum is *B*. Unobserved reflections were given zero weight in the refinement. The phosphorus and sulphur atoms were corrected for anomalous dispersion; these correction factors and the scattering factors for all atoms were taken from ref. 11*a*. We are grateful to Dr. F. R. Ahmed [11b] and his associates for use of their computer programs. The atomic parameters are given in Table 1. Observed and calculated structure factors, together with thermal parameters, are listed in Supplementary Publication No. SUP 23243 (8 pp.).†

TABLE 1

Final positional (fractional co-ordinates) parameters, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
S(1)	0.080 47(7)	−0.141 47(3)	0.375 07(13)
S(2)	0.067 83(8)	−0.116 37(10)	0.098 86(13)
S(3)	−0.023 59(6)	−0.047 11(7)	0.320 20(11)
P(1)	0.074 79(6)	0.115 73(7)	0.296 91(10)
P(2)	0.244 04(7)	0.082 05(8)	0.292 68(12)
P(3)	0.182 79(7)	0.215 93(8)	0.455 82(12)
F(1)	0.035 95(16)	0.162 44(18)	0.169 70(26)
F(2)	0.286 42(19)	−0.004 30(21)	0.343 75(39)
F(3)	0.301 11(17)	0.098 90(22)	0.169 69(32)
F(4)	0.201 41(19)	0.316 96(20)	0.438 01(36)
F(5)	0.184 09(19)	0.212 58(23)	0.612 92(27)
N(1)	0.118 28(23)	−0.155 93(26)	0.220 52(39)
N(2)	0.014 08(22)	−0.068 74(27)	0.154 28(38)
N(3)	0.000 09(19)	0.053 27(23)	0.355 41(35)
N(4)	0.153 33(20)	0.060 55(24)	0.242 30(35)
N(5)	0.258 52(21)	0.159 12(27)	0.401 00(39)
N(6)	0.093 05(21)	0.194 72(22)	0.404 13(37)

RESULTS AND DISCUSSION

The molecule shown in Figure 1 consists of a cyclotriphosphazene ring bonded through a bridging nitrogen atom to a five-membered S_3N_2 ring with an angle of 57°

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† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

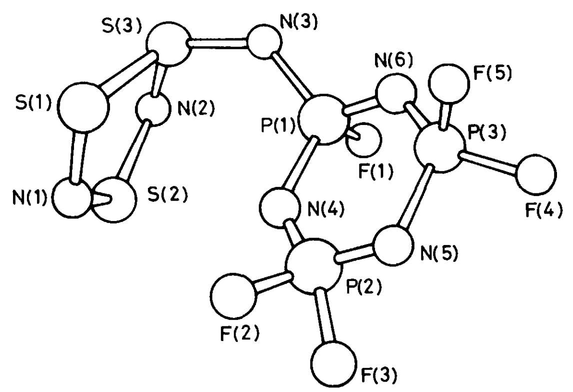

FIGURE 1 Molecular structure of $S_3N_2NP_3N_3F_5$ showing atomic numbering sheme

between the mean planes of these rings. The bond distances and angles are given in Table 2.

The N–S_3N_2 part of the molecule is similar to the $S_3N_2Cl^+$ cation [2] except that the exocyclic sulphur-nitrogen bond involves substantial π character. Both the S–N and P–N distances for the bridging nitrogen atom are considerably shorter than the corresponding single bond distances. The bridging S(3)–N(3) distance of 1.555 Å is much shorter than the S–N distance (1.73 Å) [12] in S_7NH which is essentially single (there is probably weak π bonding) and approaches the length of a typical S–N double bond, *e.g.* 1.54 Å in $S_4N_4F_4$ [13] or 1.550 Å in R–S–N=S=N–S–R where R = C_6H_4Cl-*p*.[14] The bridging distance P(1)–N(3), 1.603 Å, is also short compared with the P–N single bond (1.77 Å) in NH_3–PO_3^- [15] and approaches the P(1)–N(4) and P(1)–N(6) ring distances of 1.579 and 1.582 Å respectively. The bond angle at the bridging nitrogen is 129.9°; the increase in the angle above 120° may be a steric requirement since its decrease would result in short intramolecular contacts between the two cyclic parts of the molecule [Table 2 (*c*)].

TABLE 2

Selected distances (Å) and angles (°) for $S_3N_2NP_3F_5$ with estimated standard deviations in parentheses

(*a*) Bond lengths

S(1)–S(3)	2.221(2)	P(2)–N(4)	1.555(3)
S(1)–N(1)	1.629(4)	P(2)–N(5)	1.559(4)
S(2)–N(1)	1.540(4)		
S(2)–N(2)	1.572(4)	P(3)–N(5)	1.557(4)
S(3)–N(2)	1.647(4)	P(3)–N(6)	1.554(4)
S(3)–N(3)	1.555(4)		
		P(1)–F(1)	1.540(3)
P(1)–N(3)	1.603(3)	P(2)–F(2)	1.516(3)
P(1)–N(4)	1.579(3)	P(2)–F(3)	1.519(3)
P(1)–N(6)	1.582(4)	P(3)–F(4)	1.518(3)
		P(3)–F(5)	1.525(3)

(*b*) Bond angles

S(3)–S(1)–N(1)	97.8(2)	N(5)–P(2)–F(3)	108.9(2)
N(1)–S(2)–N(2)	109.7(2)	F(2)–P(2)–F(3)	97.3(2)
S(1)–S(3)–N(2)	92.7(1)		
S(1)–S(3)–N(3)	110.8(1)	N(5)–P(3)–N(6)	119.8(2)
N(2)–S(3)–N(3)	112.0(2)	N(5)–P(3)–F(4)	109.3(2)
		N(5)–P(3)–F(5)	108.3(2)
N(3)–P(1)–N(4)	114.4(2)	N(6)–P(3)–F(4)	109.8(2)
N(3)–P(1)–N(6)	108.7(2)	N(6)–P(3)–F(5)	109.3(2)
N(4)–P(1)–N(6)	116.7(2)	F(4)–P(3)–F(5)	98.2(2)
N(3)–P(1)–F(1)	103.9(2)		
N(4)–P(1)–F(1)	106.0(2)	S(1)–N(1)–S(2)	117.6(2)
N(6)–P(1)–F(1)	106.0(2)	S(2)–N(2)–S(3)	119.7(2)
		S(3)–N(3)–P(1)	129.9(2)
N(4)–P(2)–N(5)	119.7(2)	P(3)–N(4)–P(2)	121.7(2)
N(4)–P(2)–F(2)	110.3(2)	P(2)–N(5)–P(3)	120.2(2)
N(4)–P(2)–F(3)	109.9(2)	P(1)–N(6)–P(3)	122.0(2)
N(5)–P(2)–F(3)	108.5(2)		

(*c*) Some intramolecular non-bonding contacts

S(2) · · · N(4)	3.239	N(1) · · · N(4)	3.225
S(3) · · · N(4)	3.313	N(2) · · · N(4)	3.377

(*d*) Some intermolecular distances <3.35 Å

S(1) · · · N(3^{I})	3.185	F(1) · · · F(5^{III})	3.034
S(2) · · · F(1^{II})	3.157	F(2) · · · F(4^{IV})	2.779
S(3) · · · N(3^{I})	3.170	F(3) · · · F(4^{III})	3.014
		F(4) · · · F(5^{III})	3.195

Superscripts in Roman refer to the following equivalent positions with respect to the reference molecule at x, y, z: I $-x, -y, 1-z$; II $-x, -y, -z$; III $x, \frac{1}{2}-y, -\frac{1}{2}-z$; IV $\frac{1}{2}-x, -\frac{1}{2}-y, z$.

TABLE 3

Equation of the weighted least-squares mean plane [X, Y, Z refer to orthogonal co-ordinates (Å) whose directions lie along *a*, *b*, and *c*] and distances Δ (Å) from the plane, with standard deviations σ

$$-0.4978X - 0.8635Y - 0.0810Z - 0.8569 = 0$$

	S(1)	S(2)	S(3) *	N(1)	N(2)	N(3) *
Δ	−0.003	−0.0006	−0.326	0.005	0.002	−1.810
σ	0.0012	0.0014	0.001	0.004	0.004	0.003

	P(1)	P(2)	P(3)	N(4)	N(5)	N(6)
Δ	−0.001	0.002	0.000	0.001	−0.017	0.014
σ	0.001	0.001	0.001	0.004	0.004	0.004

* Not included in the mean-plane calculation.

The S_3N_2 ring is not planar (*cf.* $S_3N_2Cl^+$); [2] S(3) lies 0.33 Å above the mean plane of the remaining four atoms in the ring (Table 3). The maximum deviation of these atoms from their mean plane is 0.005 Å. The S–N bond lengths are all shorter than the normal single bond length of 1.73 Å and indicate substantial multiple bonding around the ring. The S–S distance (2.22 Å) is probably short enough to allow significant π bonding (*cf.* 2.18 Å in $S_3N_2Cl^+FeCl_4^-$) [16] despite some lengthening due to cyclic strain.[17]

A comparison of the S–N bond distances observed in a selection of S_3N_2 ring compounds is shown in Table 4. This demonstrates that the average S–N bond distance which varies from 1.59 to 1.60 is insensitive to the substituent attached to the ring. Consequently, these overall changes cannot account for the increase in kinetic stability of $S_3N_2NP_3N_3F_5$ over $S_3N_2NSO_2F$ and $S_3N_2NC(O)CF_3$. The kinetic stability is probably related to the resistance of the substituent group to nucleophilic attack.

The cyclophosphazene portion of the molecule may be viewed as a derivative of $P_3N_3F_6$ in which one fluorine has been replaced by a nitrogen. This substitution results in a loss of the ring planarity of $P_3N_3F_6$; the latter shows 3*mm* symmetry within experimental error. The atoms in the P_3N_3 ring deviate up to 0.017 Å from their mean plane as shown in Table 3. The ring distances may be considered in two groups, those involving

TABLE 4

Bond lengths (Å) of S_3N_2X compounds

	$S_3N_2NP_3N_3F_5$	$S_3N_2Cl_2$	$S_3N_2NSO_2F$	$S_3N_2NC(O)CF_3$	$S_3N_2{}^+SO_3CF_3{}^-$
S(1)–S(3)	2.221(2)	2.136(5)	2.200(2)	2.206(1)	2.138(2)
S(1)–N(1)	1.629(4)	1.615(5)	1.635(3)	1.633(2)	1.612(5)
S(2)–N(1)	1.540(4)	1.543(5)	1.565(3)	1.551(2)	1.575(5)
S(2)–N(2)	1.572(4)	1.617(5)	1.578(3)	1.589(3)	1.562(5)
S(3)–N(2)	1.647(4)	1.581(5)	1.644(3)	1.641(4)	1.617(5)
S(3)–N(3)	1.555(4)	——	1.603(3)	1.600(2)	——
Average (S–N)	1.59	1.59	1.60	1.60	1.59

P(1) and those which do not. The P–N distances not involved in P(1) are identical within experimental error, mean value 1.553(2) Å, and do not differ significantly from that of 1.560(6) Å found in $P_3N_3F_6$.[18] The P–N distances involving P(1) are substantially longer, mean value 1.581 Å. Similarly all the P–F distances [apart from that to P(1)] are the same within experimental error, mean 1.520(2) Å, and this mean does not differ significantly from that [1.521(5) Å] in $P_3N_3F_6$. The longer P(1)–F(1) distance of 1.540(3) Å is probably caused by the lower electronegativity of nitrogen as compared with fluorine.

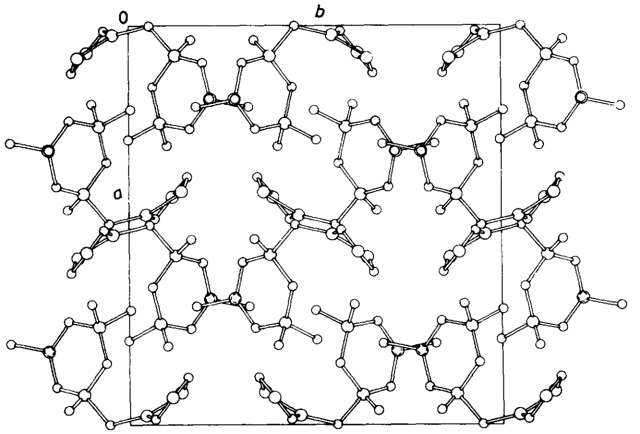

FIGURE 2 The packing of $S_3N_2NP_3N_3F_5$ viewed in projection along *c*

The packing of the molecules is shown in Figure 2 where the structure is viewed in projection along the *c* axis. There are only two S ··· N intermolecular contacts less than the normal van der Waals distance of 3.35 Å;[19] these are S(1) ··· $N(3^{I})$ at 3.185 Å and S(3) ··· $N(3^{I})$ at 3.170 Å [Table 2(*d*)]. There is one S ··· F intermolecular contact less than the van der Waals distance of 3.27 Å that is S(2) ··· $F(1^{II})$ of 3.157 Å.

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