Studies on Sulphur–Nitrogen Compounds. Part II.† Molecular and Crystal Structure of Triphenylphosphine Trisulphur Tetranitride

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The crystal structure of the title compound (I) has been solved by Patterson and heavy-atom Fourier methods and refined by full-matrix least-squares methods from single-crystal *X*-ray diffractometer data to a final *R* of 3·2% (1552 observed reflections). Crystals are monoclinic, space group $P2_1/a$, with $a = 14{\cdot}978(10)$, $b = 13{\cdot}107(6)$, $c = 11{\cdot}588(8)$ Å, $\beta = 124{\cdot}84(3)°$, with $Z = 4$. The triphenylphosphine group is bonded through nitrogen to an alternating S_3N_3 ring, five members of which are planar.

MUCH attention has been paid to determination of the presence or absence of aromaticity and description of the orbital arrangement in alternating sulphur–nitrogen cyclic structures.[1] Thus discussion of the p_π–d_π orbital overlap and the geometries that might be permitted by such situations,[2] the applicability of the Hückel rule to cyclic systems, and the interpretation of the appearance of planarity or nonplanarity,[3] have been a part of the focus of research in this area.

However, the growing number of single-crystal *X*-ray studies of sulphur–nitrogen materials, both open-chain and cyclic, S_nN_n and S_nN_m, provide evidence for another approach to bonding. There is a correlation of the angle at sulphur in an N–S–N configuration with the S–N bond length (Table 1).[4-12]

TABLE 1

Sulphur–nitrogen bond lengths and angles at sulphur in structures containing N–S–N

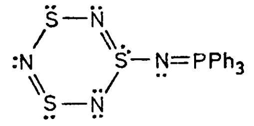
Compound	S–N/Å		Angle/°	
S_4N_4 [a]	1·596—1·634		103—105	
$S_4N_4H_4$ [b]	1·667—1·682		108	
$S_5N_5^+AlCl_4^-$ [c]	(1·519—1·583)		108·4—110·2	
		1·453—1·589		117·9—116·8
$(Cl_5Sb)_2N_2S_2$ [d]	1·616, 1·623		84·9	
$(NSOCl)_3$ [e,f]		1·564		113·0
$S_4N_3^+NO_3^-$ [g]		1·493—1·582		119·0—118·8
p-Cl·C_6H_4·SNSNS·C_6H_4-*p*-Cl [h]		1·593, 1·561		124·1
	1·657, 1·662		100, 100	
$Ph_2CNSNSNSNCPh_2$ [i]		1·546		124·22
	1·647		96·75	

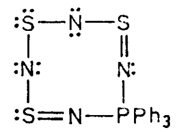
[a] Ref. 4. [b] Ref. 5. [c] Ref. 6. [d] Ref. 7. [e] Ref. 8. [f] Ref. 9. [g] Ref. 10. [h] Ref. 11. [i] Ref. 12.

There are some exceptions to this pattern of S–N bonds in the longer range subtending angles at sulphur in the shorter range. $S_5N_5^+AlCl_4^-$ has three relatively large angles at sulphur and relatively shorter bonds from nitrogen atoms to those sulphur atoms, but it also has two other sulphur atoms with relatively smaller angles and the bonds between them and the adjacent nitrogen atoms do not fall in the larger range, as in the other structures.

There are three other sulphur–nitrogen materials whose structures reveal inconsistencies with this pattern. The two studies of the $S_3N_2Cl^+$ ion show the angle at the central sulphur to be 106·3—105·8° and one of the bonds to nitrogen to be in the longer range (1·617 and 1·604 Å), while the other is in the shorter range (1·546 and 1·543).[13,14] $(NSF)_4$ Shows a relatively large angle at sulphur (117·7°) and alternating S–N bonds of 1·660 and 1·540 Å.[15]

Fluck *et al.*[16] treated triphenylphosphine with tetrasulphur tetranitride, observing that while the final sulphur-containing product was triphenylphosphine sulphide, the reaction proceeded through a relatively stable intermediate, isolated as a red crystalline solid of


(I)


(II)

molecular formula $S_3N_4PPh_3$. Two possible structures (I) and (II) were suggested. In order to show that the

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† Part I, ref. 12.

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structure was (I) and to provide further information about S–N bonding distances and the angles at sulphur, the crystal and molecular structure of triphenylphosphine trisulphur tetranitride * was determined.

EXPERIMENTAL

Crystal Data.—$(C_6H_5)_3PN_4S_3$, $M = 414{\cdot}4$, Monoclinic, $a = 14{\cdot}978(10)$, $b = 13{\cdot}107(6)$, $c = 11{\cdot}588(8)$ Å, $\beta = 124{\cdot}84(3)°$, $U = 1867{\cdot}1$ Å^3, $D_m = 1{\cdot}45$ (by flotation), $Z = 4$, $D_c = 1{\cdot}47$. Space group $P2_1/a$ from systematic absences: $h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$. Mo-K_α radiation, $\lambda = 0{\cdot}70926$ Å; μ(Mo-K_α) = 5·06 cm^{-1}.

The compound was prepared according to ref. 16 and recrystallized from benzene as bright red-orange trapezoids. The space group was determined from preliminary Weissenberg and precession photographs. A crystal of maximum dimension 0·3 mm was mounted on a Picker automated four-circle diffractometer. Cell constants were determined during alignment procedures by least-squares refinement of the setting angles of 12 high-angle reflections which were carefully centred. Molybdenum-K_α radiation was used for data collection of all independent reflections to sin $\theta_{max.}$ 0·4942. A θ—2θ scan was used over a range of 1·66° at 1° min^{-1}. Background measurements were made for 10 s each on either side of the calculated peak angle. Three standard reflections, monitored every 50 reflections, had net counts constant to within 5% over the whole data measurement period. Of the 2106 reflections measured, 1552 were classed as observed after Lorentz and polarization corrections were applied, according to the criterion $|F_o|/\sigma|F_o| > 1{\cdot}0$. No absorption corrections were made.

TABLE 2

Position and thermal parameters * (all $\times 10^4$)

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	3019(2)	3375(2)	1195(3)	43(2)	48(2)	88(4)	4(2)	22(2)	1(2)
S(1)	4477(2)	2711(2)	2390(3)	59(2)	46(2)	113(4)	−5(2)	33(3)	−10(2)
S(2)	6590(3)	3308(3)	4543(4)	65(3)	116(4)	104(5)	−9(3)	13(3)	−7(3)
S(3)	6005(3)	3047(3)	1763(4)	81(4)	115(4)	166(6)	−28(3)	64(4)	−41(4)
N(1)	3309(7)	3198(8)	1796(10)	41(8)	88(9)	138(15)	−9(6)	49(9)	6(9)
N(2)	4757(8)	3071(8)	1210(10)	94(10)	75(8)	56(12)	−4(7)	29(9)	−5(8)
N(3)	5337(8)	3308(8)	3945(9)	79(10)	80(9)	76(12)	−32(7)	33(9)	−23(8)
N(4)	6857(10)	3236(9)	3459(13)	79(11)	88(11)	219(22)	3(9)	−8(13)	−51(13)
C(1)	4155(9)	5265(8)	1873(12)	48(9)	30(7)	107(16)	7(6)	12(11)	9(9)
C(2)	4666(10)	5423(9)	1212(12)	61(11)	59(10)	138(19)	8(8)	48(13)	37(11)
C(3)	5620(8)	6020(9)	1920(12)	35(9)	71(10)	104(17)	−10(8)	24(10)	16(10)
C(4)	6034(9)	6461(10)	3274(15)	51(11)	77(11)	173(22)	10(8)	68(14)	17(12)
C(5)	5474(11)	6299(10)	3890(12)	76(12)	68(10)	81(16)	10(9)	−1(12)	−4(10)
C(6)	4507(9)	5695(8)	3280(11)	66(10)	36(8)	74(15)	0(7)	4(10)	−8(9)
C(7)	2080(8)	4858(9)	1556(12)	30(8)	64(10)	103(16)	2(7)	12(10)	−18(10)
C(8)	2073(11)	4318(9)	2672(13)	80(12)	54(9)	118(18)	−6(8)	39(12)	0(10)
C(9)	1342(11)	4677(13)	3030(17)	59(12)	131(17)	228(28)	−22(11)	64(16)	−54(18)
C(10)	738(11)	5593(12)	2343(17)	41(11)	104(14)	237(30)	−22(10)	35(16)	−62(17)
C(11)	746(11)	6087(11)	1214(15)	73(13)	74(12)	178(24)	−6(10)	43(15)	0(14)
C(12)	1487(11)	5736(10)	849(14)	73(12)	64(11)	160(22)	17(9)	18(14)	−16(12)
C(13)	2325(8)	4364(9)	9322(11)	24(8)	72(8)	105(16)	7(7)	32(9)	−15(10)
C(14)	1245(10)	4235(12)	6396(13)	41(10)	129(15)	108(18)	−22(10)	27(11)	−46(14)
C(15)	1527(9)	5264(12)	7040(13)	29(9)	158(17)	112(18)	3(10)	32(11)	21(14)
C(16)	2130(8)	5313(9)	8605(11)	21(9)	108(11)	97(15)	2(7)	36(9)	14(10)
C(17)	2007(8)	3363(10)	8669(12)	30(8)	102(12)	130(17)	−6(8)	45(10)	−49(12)
C(18)	1494(9)	3353(11)	7194(14)	38(10)	114(13)	166(23)	−28(9)	51(13)	−36(14)

Computation was performed using the programs of ref. 17 for Patterson, electron-density, and difference electron-density maps, of ref. 18 for full-matrix least-squares, and ref. 19 for molecular geometry; scattering factors were taken from ref. 20.

Determination of the Structure and Refinement.—The three sulphur atoms and the phosphorus atom were located from the three-dimensional Patterson map computed with all observed data. Three cycles of least-squares refinement of the scale factor, positional parameters, and isotropic temperature factors for the four atoms gave R 49·3% for all observed reflections. Successive difference-Fourier–least-squares cycles allowed location of the four nitrogen atoms and the eighteen carbons (R 14·7). At this point a difference-Fourier showed the presence of thermal anisotropic motion and the isotropic temperature factors were converted to their anisotropic equivalents. Three least-squares cycles of refinement of all parameters reduced R to 10·7%. A weighting scheme was introduced to down-weight the observations of highest intensity such that for scaled $|F_o| > 28{\cdot}9$, the weight was $(28{\cdot}9/|F_o|)^2$. Unit weights were used for all other observations. At the conclusion of the analysis the values of $>\Sigma(|F_o| - |F_c|)^2$ for the reflections grouped in 17 sets of increasing $|F_o|$ did not differ by more than a factor of 1·6. The maximum shift-to-σ ratio of a parameter was 0·02 and refinement was terminated. The final R was 3·2%. No attempt was made to locate protons. A final difference-Fourier showed no peak $>0{\cdot}2$ eÅ^{-3}. Calculated and observed structure factors are listed in Supplementary Publication No. SUP 21049 (4 pp.).†

DISCUSSION

A projection of the structure on the *ab* plane based on the position parameters of Table 2 may be seen in the

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* 1-[(Triphenylphosphoranylidene)amino]-1,3,5-trithia-2,4,6-triazine.

† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full-size copies).

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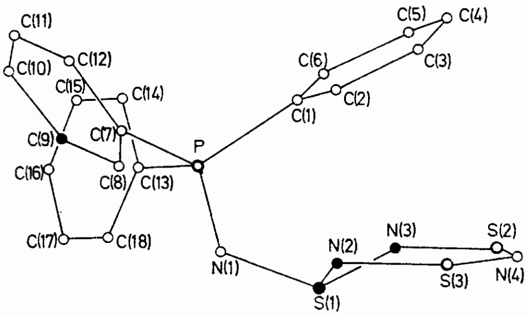
Figure. Table 2 also gives thermal parameters, and Table 3 bond lengths, non-bonded distances, and angles.



Projection of the structure on the *ab* plane

The structure has five members of the S_3N_3 ring [N(2)–S(3)–N(4)–S(2)–N(3)] lying on a plane (maximum deviation 0·035 Å) and the bonds to the remaining sulphur [S(1)] defining a plane which forms a dihedral angle of 139(1·5)° with the plane of the five atoms.[21]

TABLE 3

Bond lengths and angles

(*a*) Distances (Å)			
P–N(1)	1·645(10)	P–C(13)	1·792(3)
N(1)–S(1)	1·602(10)	C(1)–C(2)	1·37(2)
S(1)–N(2)	1·667(10)	C(2)–C(3)	1·41(1)
S(1)–N(3)	1·693(10)	C(3)–C(4)	1·42(2)
N(2)–S(3)	1·608(11)	C(4)–C(5)	1·39(2)
S(3)–N(4)	1·639(13)	C(5)–C(6)	1·42(2)
N(4)–S(2)	1·522(16)	C(6)–C(1)	1·40(1)
S(2)–N(3)	1·589(10)	C(7)–C(8)	1·42(2)
P–S(1)	2·826(4)	C(8)–C(9)	1·42(2)
N(2)–N(3)	2·739(13)	C(9)–C(10)	1·43(2)
N(2)–N(4)	2·702(15)	C(10)–C(11)	1·39(2)
N(4)–N(3)	2·643(18)	C(11)–C(12)	1·41(2)
S(2)–S(3)	2·833(6)	C(12)–C(7)	1·40(2)
S(3)–S(1)	2·806(5)	C(13)–C(14)	1·42(2)
S(1)–S(2)	2·800(5)	C(14)–C(15)	1·41(2)
N(1)–N(2)	2·589(14)	C(15)–C(16)	1·40(1)
N(1)–N(3)	2·610(13)	C(16)–C(17)	1·39(2)
P–C(1)	1·831(12)	C(17)–C(18)	1·42(2)
P–C(7)	1·793(12)	C(18)–C(13)	1·43(2)
(*b*) Angles (°)			
P–N(1)–S(1)	121·0(6)	N(1)–P–C(7)	105·7(7)
N(1)–S(1)–N(2)	104·7(5)	N(1)–P–C(1)	117·4(5)
N(1)–S(1)–N(3)	104·7(5)	N(1)–P–C(13)	109·6(4)
N(3)–S(1)–N(2)	109·2(5)	C(1)–P–C(7)	109·6(6)
S(1)–N(2)–S(3)	117·9(6)	C(1)–P–C(13)	106·2(4)
N(2)–S(3)–N(4)	112·7(7)	C(7)–P–C(13)	107·1(4)
S(3)–N(4)–S(2)	127·3(9)	N(2)–N(3)–N(4)	60·2(4)
N(4)–S(2)–N(3)	116·3(6)	N(3)–N(4)–N(2)	61·6(4)
S(2)–N(3)–S(1)	117·1(6)	N(4)–N(2)–N(3)	58·1(4)

Planarity in sulphur–nitrogen structures containing multiple N–S–N configuration occurs in some cases and not in others as shown by single-crystal *X*-ray studies. Of those structures which are not planar, S_4N_4, $S_4N_4H_4$, and $S_4N_4F_4$ exist in unexpectedly differing structures considering their close chemical relationship. S_4N_4 Exists as a cage structure with the four nitrogen atoms roughly coplanar and the bridging sulphurs alternately above and below that plane.[4] The compounds $S_4N_4H_4$ (ref. 5) and $S_4N_4F_4$ (ref. 15) exist as regularly puckered rings but without the coplanarity of the sulphur atoms. $(NSOCl)_3$ (refs. 8 and 9) and $(NSCl)_3$ (ref. 9) contain chair-shaped six-membered rings of alternating sulphur and nitrogen atoms. $S_3N_2Cl^+Cl^-$ Exists with the two nitrogen atoms 0·140 and 0·188 Å above and below the plane of the three sulphur atoms.[13,14] The compound $S_5N_5^+AlCl_4^-$ exists as a heart-shaped alternating sulphur–nitrogen ring, nearly planar, the maximum deviation from the plane being 0·039 Å.[6] The S_2N_2 ring of $(Cl_5Sb)_2N_2S_2$ is planar [7] as is the sulphur–nitrogen portion of $S_4N_3^+NO_3^-$ [10] (maximum deviation 0·023 Å). Two open-chain materials have been studied; *p*-Cl·C_6H_4·SNSNS·C_6H_4-*p*-Cl shows the central SNSNS chain to be planar with the bonded carbons of the *p*-chloro-group 0·22 and 0·10 Å from that plane.[14] The *X*-ray study of $Ph_2CNSNSNSNCPh_2$ shows that only the control SNSNS chain is planar (maximum deviation 0·02 Å), the terminal nitrogen atoms being 0·55 Å from that plane.[12] Thus sulphur–nitrogen compounds exhibit structures which are not necessarily predictable in their planarity or nonplanarity. However, considering the relief of angle strain that would occur with the removal of even a single atom from the plane in (I), it is unexpected that five members of the S_3N_3 ring should be planar. The sixth member of the ring [S(1)] is trivalent and would not be expected to employ the same bonding orbital arrangement as a sulphur bonded to only two other atoms. Thus it is not surprising that it is not a part of the planar system.

The shortest sulphur–sulphur distance of 2·800(5) Å is somewhat longer than the non-bonded distance (2·58 Å) [4] in S_4N_4 but still shorter than the mean (2·927 Å) [5] in $S_4N_4H_4$, and shorter than the sum of van der Waals radii (3·50—3·53 Å).

Bonding about the phosphorus atom is roughly tetrahedral with angles ranging from 105·7—117·4°.

Examination of the bond lengths and the angles at sulphur reveals that the trivalent sulphur [S(1)] has N–S–N angles in the shorter range (104·7, 104·7, and 109·2°) and bonds to nitrogen in the longer range (1·602, 1·693, and 1·667). Sulphur S(3) is somewhat less definite with a N–S–N 112·7° and bonds of 1·608 and 1·639 Å. It would seem to fall in the same class as S(1).

The remaining sulphur S(2) has a larger angle at sulphur (116·3°) and distances in the shorter range 1·589 and 1·522 Å. Thus like the open-chain materials whose structures have been studied, (I) shows both types of sulphur–nitrogen bonding in the same molecule. The bonding behaviour of the three sulphur atoms, despite their different co-ordinations, is consistent with the pattern observed in other sulphur–nitrogen structures.

[3/2574 *Received, 20th December*, 1973]

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