Studies on Sulphur–Nitrogen Compounds. Part 3.† Crystal and Molecular Structure of Triphenylarsine–Trisulphur Tetranitride (1/1)

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The crystal structure of triphenylarsine–trisulphur tetranitride (1/1) has been solved from diffractometer X-ray single-crystal data by heavy-atom methods and refined by full-matrix least-squares methods to a final R of 5.0 for 2324 observed reflections. Crystals are of space group $P2_1/n$ with unit cell dimensions a = 12.860(11), b = 13.259(11), c = 11.786(12) Å, β = 103.33(6)°, and Z = 4. The triphenylarsine group is bonded through nitrogen to an $(SN)_x$ ring, five members of which are planar.

A REVIEW of the structures of materials containing a series of sulphur–nitrogen bonds between two-co-ordinate sulphur and sp^2 hybridized nitrogen shows them all to be planar and characterized by angles larger than 120° at nitrogen atoms whose S–N bonds are part of the planar system.[1-12] S_2N_2 is considered an exception because of the obvious impossibility of 120° angles at nitrogen. N–S–N angles where both S–N bonds are part of the planar system vary from 108—124° and sulphur–nitrogen bond lengths vary from 1.45—1.63 Å as compared with the accepted sulphur–nitrogen single-bond length of 1.74 Å (Table 1 and Figure 1). Both ring and chain systems fit into this generalization.

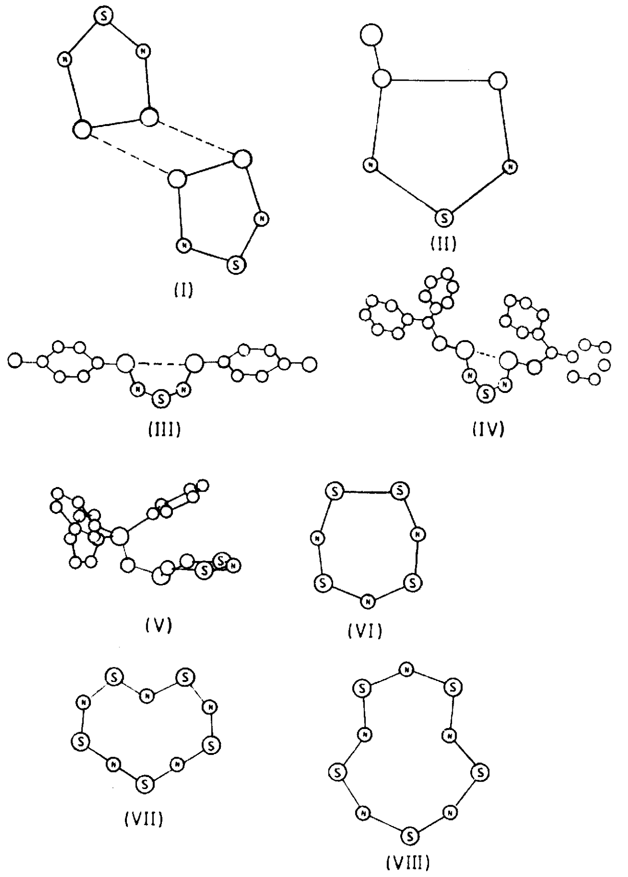

FIGURE 1 Structures of the planar sulphur–nitrogen materials of Table 1

Omitted from this group is S_4N_4 whose sulphur–sulphur distance of 2.576 Å as compared to the sulphur–sulphur single bond length of 2.39 Å in $[S_2O_4]^-$ and the sum of the van der Waals radii (3.7 Å) show it to have three-co-ordinate sulphur atoms.[1] Similarly $[NH_4]$-$[S_4N_5O]$, where two seemingly two-co-ordinate sulphur atoms have a sulphur–sulphur distance of 2.633 Å, is not included.[2] $[SN]_x$, which is reported to be a planar chain structure, is omitted because full structural details of the packing of the interchain contact distances to sulphur have not been published and thus the actual two-co-ordination of sulphur has not been established.[3]

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† Part 2 is ref. 10.

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Inasmuch as the configuration of $[S_5N_5]^+$ varies with the nature of the anion,[4] and the configuration of five members of the S_3N_3 ring of $Ph_3PS_3N_4$ was planar with the remaining sulphur 139° from that plane, the structure of $Ph_3AsS_3N_4$ was of interest.[5] We wished to observe the effect of substitution of arsenic for phosphorus on the bonding and structure of the sulphur–nitrogen system.

TABLE 1

Planar sulphur–nitrogen structures; bond lengths (Å) and angles (°)

Compound	Cpd. No.	S–N	S–N–S	N–S–N
$[S_3N_2][S_2O_6Cl]$ [a]	(I)	1.569, 1.605 [b]		108
$[S_3N_2Cl][FeCl_4]$ [c]	(II)	1.604, 1.546		105.8
$[S_3N_2Cl]Cl$ [d]		1.617, 1.543		106.3
S_2N_2 [e]		1.651, 1.657	90.42	89.58
$(p\text{-}ClC_6H_5)_2S_3N_2$	(III)	1.539, 1.561		124
		1.662, 1.561	126.0	
		1.539, 1.657	129.0	
$Ph_2CNSNSNSNCPh_2$ [g]	(IV)	1.546, 1.546		124.2
		1.546, 1.657	126.4	
$Ph_3PS_3N_4$ [h]	(V)	1.608, 1.639		112.7
		1.639, 1.522	127.3	
		1.522, 1.589		116.3
$[S_4N_3][NO_3]$ [i]	(VI)	1.582, 1.493	153.3	
		1.493, 1.544		119.0
		1.544, 1.579	134.4	
		1.579, 1.550		118.8
		1.549, 1.550	151.5	
$[S_5N_5][AlCl_4]$ [j]	(VII)	1.548, 1.550		108.4
		1.550, 1.569	128.4	
		1.569, 1.519		110.2
		1.519, 1.566	138.4	
		1.566, 1.481		117.5
		1.481, 1.523	177.4	
		1.523, 1.453		116.8
		1.453, 1.589	178.3	
		1.589, 1.583		117.9
		1.583, 1.548	138.2	
$[S_5N_5][Cl_3POSnCl_5]$ [k]	(VIII)	1.581, 1.497		111.1
		1.581, 1.587	131.5	
		1.587, 1.535		109.9
		1.535, 1.568	135.5	
		1.568, 1.553		110.1
		1.553, 1.563	148.1	
		1.563, 1.567		124.6
		1.567, 1.566	153.9	
		1.566, 1.557		112.6
		1.557, 1.497	146.1	

[a] Ref. 6. [b] Sulphur–nitrogen distances given but not located on the ring. [c] Ref. 7. [d] Ref. 8; slightly puckered. [e] Ref. 3. [f] Ref. 9. [g] The terminal nitrogen atoms of this system are 0.55 Å from the plane; ref. 10. [h] Ref. 5. [i] Ref. 11. [j] Ref. 12. [k] Ref. 4.

EXPERIMENTAL

Crystal Data.—$C_{18}H_{15}AsN_4S_3$, $M = 458.46$, Monoclinic, $a = 12.860(11)$, $b = 13.259(11)$, $c = 11.786(12)$ Å, $\beta = 103.33(6)°$, $D_m = 1.58(3)$ g cm^{-3} by flotation, $Z = 4$, $D_c = 1.557(6)$ g cm^{-3}. Space group $P2_1/n$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 21.5 cm^{-1}.

The material was prepared by allowing a 1 : 1 mixture of $C_{18}H_{15}As$ and S_4N_4 in benzene to react, when the initially colourless solution became dark red within 30 s. Upon cooling, dark red rhombohedral crystals were precipitated. A crystal of dimensions 0.10 × 0.15 × 0.25 mm was mounted on a Picker four-circle automated diffractometer. Unit-cell dimensions were determined by a least-squares procedure during alignment. Data were obtained for all independent reflections to $\sin\theta_{\max.}$ 0.45 by a θ—2θ scan (2.4° at 1° min^{-1}). Background measurements were made for 20 s each on either side of the calculated peak angle. The net counts of 3 standard reflections measured after every 40 reflections were constant to within 4% during data collection. The intensities of 4 488 independent lattice points were measured of which 2 324 were classed as observed after data reduction ($|F_o|/\sigma|F_o| > 3.0$). Absorption corrections were not made.

Determination and Refinement of the Structure.—The positions of the three sulphur atoms and the arsenic atom were located from a three-dimensional Patterson map computed with all observed data. Three cycles of full-matrix least-squares refinement of the scale factor, position parameters, and isotropic temperature factors followed by a difference Fourier allowed location of all non-hydrogen atoms. Three cycles of refinement gave R 10.7. A difference-Fourier revealed the presence of anisotropic thermal motion and all isotropic temperature factors were converted into their anisotropic equivalents. Three cycles of full-matrix refinement of the temperature and position parameters for all atoms and the scale factor gave a final R of 5.0.[13] The maximum ratio of the shift of a parameter to its corresponding σ was 0.01. No attempt was made to locate protons. Unit weights were used throughout. A final difference-Fourier showed no peak > 0.3 eÅ^{-3}. Calculated and observed structure factors and anisotropic thermal parameters are available in microfiche as Supplementary Publication No. SUP 21881 (5 pp., 1 microfiche).*

TABLE 2

Position parameters

Atom	*X*	*Y*	*Z*
As	0.196 00(6)	0.066 38(6)	0.316 76(6)
S(1)	0.051 6(2)	0.236 4(2)	0.292 6(2)
S(2)	−0.094 7(2)	0.194 7(2)	0.078 6(2)
S(3)	−0.155 8(2)	0.165 6(2)	0.292 6(2)
N(1)	0.165 2(5)	0.196 8(5)	0.350 2(6)
N(2)	0.027 4(6)	0.196 2(5)	0.153 3(6)
N(3)	−0.032 9(6)	0.175 4(6)	0.356 9(6)
N(4)	−0.182 9(6)	0.174 3(6)	0.153 8(7)
C(1)	0.078 4(5)	−0.026 7(5)	0.280 0(6)
C(2)	0.026 6(6)	−0.044 9(6)	0.160 9(7)
C(3)	−0.064 2(7)	−0.107 5(7)	0.137 3(8)
C(4)	−0.102 5(7)	−0.152 1(7)	0.228 3(8)
C(5)	−0.049 7(6)	−0.133 9(7)	0.346 0(8)
C(6)	0.041 9(6)	−0.071 3(6)	0.371 7(6)
C(7)	0.292 5(6)	0.015 8(6)	0.456 9(6)
C(8)	0.295 7(6)	0.066 9(8)	0.561 7(7)
C(9)	0.364 0(8)	0.029 9(9)	0.665 1(8)
C(10)	0.425 0(8)	−0.055 0(9)	0.662 9(8)
C(11)	0.420 7(7)	−0.106 0(8)	0.558 0(9)
C(12)	0.353 3(7)	−0.070 5(7)	0.452 6(7)
C(13)	0.269 1(5)	0.066 1(6)	0.190 8(6)
C(14)	0.301 5(6)	0.160 6(7)	0.155 7(7)
C(15)	0.356 4(7)	0.162 4(8)	0.063 8(8)
C(16)	0.377 1(6)	0.071 2(10)	0.009 8(7)
C(17)	0.342 6(7)	−0.021 5(8)	0.045 3(7)
C(18)	0.288 0(6)	−0.024 2(6)	0.137 6(7)

DISCUSSION

A projection of the structure is shown in Figure 2 based on the positional parameters of Table 2. Figure

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue. (Items less than 10pp. are supplied as full-size copies.)

[13] Calculations were performed using the programs of W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory Reports ORNL TM 305 and ORNL CF 59 12 3, 1959; W. C. Sly, D. P. Shoemaker, and J. M. Van den Hende, Esso Research and Engineering Co., Report CBRL 22M 62. Scattering factors were taken from F. M. Moore, *Acta Cryst.*, 1963, **16**, 1169.

3 shows the packing of the molecules in a unit cell. Bond angles and distances are listed in Table 3.

TABLE 3

Bond lengths (Å) and angles (°)

(*a*) Distances			
As–N(1)	1.837(2)	S(2)–S(3)	2.835(4)
N(1)–S(1)	1.554(5)	S(1)–S(3)	2.827(3)
S(1)–N(2)	1.686(3)	N(2)–N(3)	2.700(11)
S(1)–N(3)	1.669(4)	N(2)–N(4)	2.721(12)
N(2)–S(2)	1.613(7)	N(3)–N(4)	2.706(14)
S(2)–N(4)	1.615(6)	N(1)–N(2)	2.576(13)
N(4)–S(3)	1.596(5)	N(1)–N(3)	2.583(12)
S(3)–N(3)	1.592(7)	As–C(1)	1.924(8)
As–S(1)	2.893(2)	As–C(7)	1.943(11)
S(1)–S(2)	2.831(2)	As–C(13)	1.932(9)
(*b*) Angles			
As–N(1)–S(1)	116.9(1)	S(3)–N(3)–S(1)	120.1(2)
N(1)–S(1)–N(2)	105.2(4)	N(1)–As–C(1)	117.1(2)
N(1)–S(1)–N(3)	106.4(1)	N(1)–As–C(7)	105.6(2)
N(2)–S(1)–N(3)	107.2(3)	N(1)–As–C(13)	109.5(2)
S(1)–N(2)–S(2)	118.2(4)	C(1)–As–C(7)	106.5(4)
N(2)–S(2)–N(4)	114.9(2)	C(1)–As–C(13)	108.9(4)
S(2)–N(4)–S(3)	124.0(3)	C(7)–As–C(13)	108.9(3)
N(4)–S(3)–N(3)	116.1(4)		

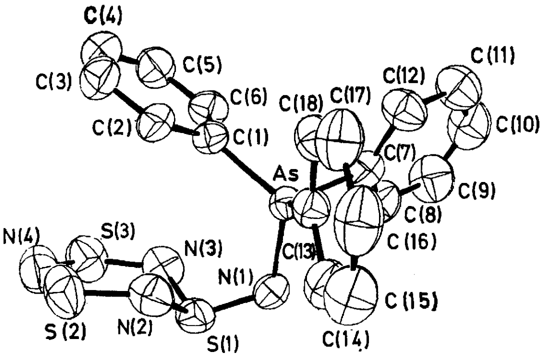

FIGURE 2 A projection of the structure

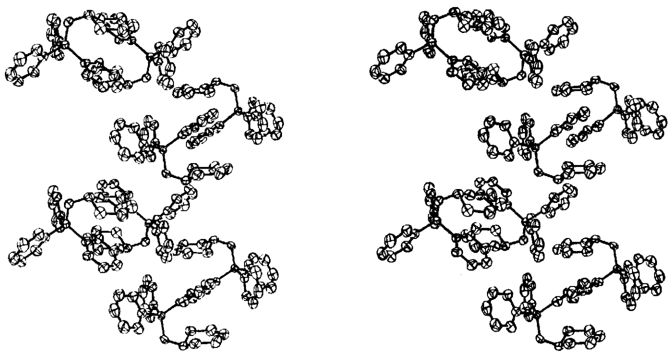

FIGURE 3 Packing of molecules in cell

The structure of triphenylarsine trisulphur tetranitride is similar to that of the analogous phosphine compound (V).[5] Both materials show the triphenyl substituent group bonded through nitrogen to the sulphur of an S_3N_3 group, the remaining five members of which are planar [maximum deviations from plane 0.037 (As) and 0.035 Å (P)]. In the triphenylarsine material the S(1),N(2),N(3) plane forms an angle of 140(1.12)° with the N(2),S(2),N(4),S(3),N(3) plane and in (V) the analogous angle is 139(1.5)°.

If one describes the exocyclic nitrogen as receiving two electrons from arsenic or phosphorus in a dative bond and using one electron to form a σ bond with sulphur, this nitrogen retains two unshared pairs of electrons. Back-donation of some part of these electrons into the vacant *d* orbitals of the adjacent sulphur or the adjacent phosphorus or arsenic atom can explain the shortening of the bonds to nitrogen.

In as much as all arguments for interaction of nitrogen 2*p* and sulphur or phosphorus 3*d* orbitals depend on ligand effects shrinking the size of the 3*d* orbital sufficiently for effective overlap with the smaller 2*p* orbital,[14] it would seem that back-donation could take place more effectively between nitrogen and phosphorus rather than arsenic which has vacant 4*d* orbitals. Thus the As–N bond (1.837 Å) approaches the As–N single-bond length [single 1.87 (ref. 15), double 1.742—1.771 Å (ref. 16)], while the P–N bond (1.645 Å) is considerably smaller. (The P–N single-bond distance is taken as 1.77 Å,[17] although that in $[NPCl_2]_5$ is 1.52 Å.)[18] It can be postulated that in (V) nitrogen back-donation takes place to phosphorus as well as to sulphur, so that the bond to sulphur is longer (however, still shorter than the S–N single bond of 1.74 Å). When interactions with arsenic are not favourable, donation to sulphur is increased and the bond becomes shorter (1.55 Å).

Bond-angle opening at sp^2-hybridized nitrogen in sulphur–nitrogen or phosphorus–nitrogen systems is commonly considered to be directly related to the amount of back-donation taking place into empty *d* orbitals on the neighbouring sulphur or phosphorus.[19] In (V) the angle at this nitrogen is larger (121°) whereas in the arsenic derivative, where the same geometry exists for the exocyclic nitrogen and the S_3N_3 ring, the angle at the exocyclic nitrogen is decreased to 116.8°. This is consistent with increased delocalization of the nitrogen unshared pairs through back donation to phosphorus in the $Ph_3PS_3N_4$ system.

The planarity of the S_2N_3 portion of the ring is typical of two-co-ordinate sulphur bonded to sp^2 hybridized nitrogen. Only the three-co-ordinate sulphur is not part of the plane, and three-co-ordinate sulphur is not usually found as part of a planar system. The angles at sulphur are typical of these systems as are those at nitrogen.

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