Studies on Sulphur–Nitrogen Compounds. Part I. Crystal and Molecular Structure of Bis(diphenylmethylene)trisulphurtetranitride

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The structure of bis(diphenylmethylene)trisulphurtetranitride has been determined and shows the central five members of the sulphur–nitrogen chain to be nearly planar. The material crystallizes in the orthorhombic space group *Pcan* with $a = 12{\cdot}590(4)$, $b = 26{\cdot}020(9)$, and $c = 7{\cdot}286(2)$ Å. Full-matrix least-squares refinement was carried out with 907 reflections to a conventional R factor of 5·8 using anisotropic temperature factors.

THE continuing discussion of aromaticity and of the means of electron delocalization in alternating sulphur–nitrogen species has caused increased interest in the single-crystal structures of materials of this type. A recent molecular orbital treatment of the cyclic species $S_3N_4^+$ confirms the 10-π-electron count for this system [1] and leads to speculation on the aromaticity of other S_xN_y species.[2] In particular if sulphur consistently provides 2-π-electrons to a delocalized system, potentially aromatic cyclic systems have been postulated to be the neutral species: S_2N_2, S_3N_4, S_4N_2, S_4N_6, S_5N_4, S_6N_6 and the cationic species: $S_2N_3^+$, $S_3N_5^+$, $S_4N_3^+$, $S_5N_5^+$, and $S_6N_7^+$.

Of these species, a number are known to be planar. S_2N_2 which represents a 6-π-electron system has been found to be a planar, nearly square ring, structure from the i.r. spectra.[3] This material is unstable and no X-ray structure determination has been done on it. However the antimony pentachloride adduct, $S_2N_2(SbCl_5)_2$ has been shown by X-ray crystallography to have a planar S_2N_2 ring with all ring angles and distances equal.[4]

The 10-π-system $S_4N_3^+NO_3^-$ has been shown by single-crystal X-ray analysis to have a cationic and planar alternating sulphur–nitrogen ring with all sulphur–nitrogen bonds equal and the sulphur–sulphur bond length equal to that of a sulphur–sulphur single bond [5] indicating that the electron delocalization does not extend to the sulphur–sulphur bond. Thus this 10-π-system is planar but with electron delocalization only along the SNSNSNS chain.

The 10-π-system S_4N_2, involving a cyclic structure with the 1,3-nitrogen atoms doubly bound to an intervening sulphur, may also be planar (i.r. and Raman spectral evidence). No X-ray work has been done on this material.[6]

The 14-π-system, $S_5H_5^+AlCl_4^-$, has been shown to have a planar and alternating ten-membered sulphur–nitrogen ring arranged in a heart shape.[7]

There are a number of cyclic sulphur–nitrogen systems whose structures have been studied, which do not obey the $4N + 2$ rule and which are not planar. Among them are the halogenated systems: $S_3N_3Cl_3$,[8] $S_4N_4F_4$,[8,9] $S_3N_3O_3Cl_3$,[8,10] and the tetrasulphur tetranitride systems: S_4N_4 [11] and $S_4N_4H_4$.[12] S_4N_4 Has a very short non-bonded sulphur–sulphur distance of 2·586 Å. Of these materials $S_3N_3Cl_3$, $S_3N_3O_3Cl_3$, S_4N_4, $S_4N_4H_4$ have all sulphur–nitrogen distances equal and $S_4N_4F_4$ has alternating sulphur–nitrogen distances.

The compound $Ph_3PS_3N_4$ has been shown by X-ray single crystal studies to have a six-membered S_3N_3 ring, five members of which are planar (S_2N_3).[13] The third sulphur of the ring is tervalent and 139° out of the plane. Considering the reduced ring strain in a non-planar system, the partial planarity of the system is unexpected. The bonds between sulphur and nitrogen are not equal.

The structure of one sulphur nitrogen chain material is known. A single-crystal study of $(p\text{-}ClC_6H_4)_2S_3N_2$ shows the five membered alternating sulphur–nitrogen chain to be planar.[14]

With this view of structural sulphur–nitrogen chemistry in mind, the structure of $(Ph_2C)_2S_3N_4$ was undertaken. It was felt that the structure of this material which did not contain a tervalent sulphur atom but which was expected to provide an example of a long alternating sulphur–nitrogen system would provide another example in the emerging picture of how sulphur–nitrogen systems behave and bond in the solid. The product of the reaction of S_4N_4 and diphenyldiazomethane,[15] this material has one of the longest conjugated sulphur–nitrogen chains known.

EXPERIMENTAL

Crystal Data.—$C_{26}H_{20}S_3N_4$, $M = 484{\cdot}5$, Orthorhombic, $a = 12{\cdot}590(4)$, $b = 26{\cdot}020(9)$, $c = 7{\cdot}286(2)$ Å, $U = 2386{\cdot}8$ Å^3, $D_m = 1{\cdot}28$ by flotation, $Z = 4$, $D_c = 1{\cdot}26$.

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Space group *Pcan*, Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 23·3 cm^{-1}.

The material was prepared according to the method of Fluck [15] in a crystalline form suitable for *X*-ray structure analysis. A platelet, rectangular in shape and of dimensions 0·165, 0·06, and 0·42 mm, was mounted on a Picker four-circle automated diffractometer. The unit cell dimensions were determined by least squares procedures during alignment. Data were measured at 25 °C, all independent reflections to $\sin\theta_{max.} = 0{\cdot}8942$ being sampled 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. Three standard reflections were measured after every 40 reflections, their net counts being constant to within 5% over the whole data measurement period. The intensities of 1709 independent lattice points were measured of which 907 were classed as observed after data reduction. ($|F_o|/\sigma|F_o| > 1{\cdot}5$) Absorption corrections were neglected.

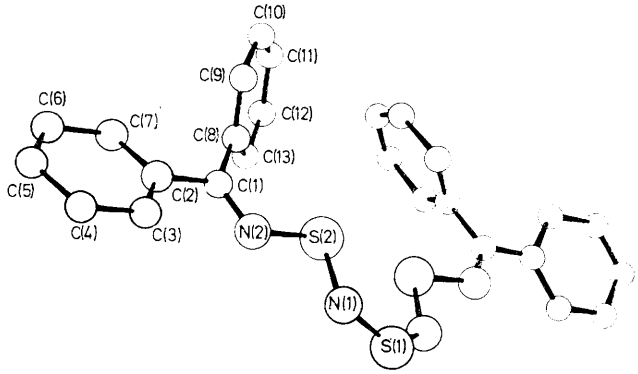
TABLE 1

Position parameters for the structure $[(C_6H_5)_2CNSN]_2S$

The estimated standard deviations are given in units of the last significant figure in the parameter itself.

Atom	*x*	*y*	*z*
S(1)	−0·1756(2)	0·0000	0·2500
S(2)	0·0120(1)	0·0548(1)	0·3532(2)
N(1)	−0·1182(4)	0·0469(2)	0·3344(9)
N(2)	0·0098(5)	0·1187(2)	0·3849(7)
C(1)	0·0991(6)	0·1426(2)	0·4078(9)
C(2)	0·0937(6)	0·1988(2)	0·4472(10)
C(3)	−0·0032(7)	0·2206(3)	0·5043(11)
C(4)	−0·0066(8)	0·2739(3)	0·5408(12)
C(5)	0·0839(8)	0·3049(3)	0·5167(13)
C(6)	0·1797(7)	0·2825(3)	0·4602(14)
C(7)	0·1851(6)	0·2291(3)	0·4243(12)
C(8)	0·2037(5)	0·1174(2)	0·4008(10)
C(9)	0·2683(7)	0·1180(3)	0·5557(14)
C(10)	0·3681(8)	0·0927(4)	0·5505(18)
C(11)	0·3987(8)	0·0680(4)	0·3906(23)
C(12)	0·3351(8)	0·0675(3)	0·2351(20)
C(13)	0·2348(6)	0·0928(3)	0·2376(14)

Determination of the Structure and Refinement.—The structure was solved by conventional heavy atom techniques and refined by full matrix least squares cycles to an *R* of 11·7% ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) for all non-hydrogen atoms with isotropic temperature factors. A difference map at this point indicated the presence of thermal anisotropic motion, consequently the isotropic temperature factors were converted to their anisotropic equivalents and refined with the position parameters for three further cycles (*R* 5·8%). The maximum ratio of the shift of a parameter to its corresponding estimated standard deviation was 0·015 and no further refinement was undertaken. No attempt was made to locate hydrogen atoms. A final difference map showed no peak higher than 0·4 eÅ^{-3}. Unit weights were used until the final cycle of least squares where reflections $|F_o| < 30{\cdot}0$ were given unit weight and those with $|F_o| > 30{\cdot}0$ were weighted $(30{\cdot}0/|F_o|)^2$. At the conclusion of the analysis, the values of $<\Sigma(|F_o| - |F_c|)^2$ for the reflections grouped in 20 sets of increasing $|F_o|$ did not differ by more than a factor of 2·8.



Projection of bis(diphenylmethylene)trisulphurtetranitride

DISCUSSION

A projection of the structure may be seen in the Figure based on the position parameters in Table 1. Table 2 gives the thermal parameters for the structure and Tables 3 and 4 the bond lengths and angles respectively. The structure factors are available in Supplementary Publication No. SUP 20986 (3 pp.).*

TABLE 2

Thermal parameters for the structure $[(C_6H_5)_2CNSN]_2S$. In the form exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{13}hl + 2\beta_{23}kl + 2\beta_{12}hk)]$

Estimated standard deviations are given in parentheses in units of the last significant figure in the parameter itself

Atom						
S(1)	0·0046(2)	0·0013(1)	0·0241(7)	0·0000	0·0000	−0·0009(1)
S(X)	0·0058(1)	0·0011(1)	0·0124(4)	0·0000(1)	−0·0007(2)	−0·0003(1)
N(1)	0·0060(4)	0·0013(1)	0·018(2)	−0·0001(2)	0·0001(6)	−0·0004(3)
N(2)	0·0074(4)	0·0012(1)	0·011(1)	−0·0002(2)	−0·0007(6)	0·0000(3)
C(1)	0·0075(6)	0·0015(1)	0·006(2)	−0·0003(2)	0·0007(7)	0·0003(3)
C(2)	0·0082(6)	0·0012(1)	0·010(2)	−0·0002(2)	−0·0016(8)	0·0001(4)
C(3)	0·0092(6)	0·0016(1)	0·016(2)	0·0011(3)	0·0003(8)	−0·0006(4)
C(4)	0·0122(8)	0·0018(1)	0·019(2)	0·0003(3)	−0·001(1)	−0·0006(4)
C(5)	0·0118(9)	0·0015(2)	0·022(2)	0·0002(3)	−0·003(1)	−0·0007(5)
C(6)	0·0110(8)	0·0016(1)	0·024(2)	0·0001(3)	−0·004(1)	0·0001(5)
C(7)	0·0088(7)	0·0014(1)	0·018(2)	−0·0004(2)	−0·004(1)	0·0006(4)
C(8)	0·0063(6)	0·0012(1)	0·016(2)	−0·0003(2)	−0·001(1)	0·0008(4)
C(9)	0·0081(7)	0·0014(1)	0·033(3)	−0·0004(2)	−0·004(1)	0·0022(5)
C(10)	0·0093(9)	0·0018(2)	0·047(4)	−0·0007(3)	−0·003(1)	0·0030(7)
C(11)	0·0081(8)	0·0017(2)	0·062(5)	−0·0002(3)	0·003(2)	0·0023(8)
C(12)	0·0087(8)	0·0017(2)	0·051(4)	−0·0006(3)	0·007(2)	0·0007(7)
C(13)	0·0084(7)	0·0014(1)	0·029(2)	−0·0008(2)	0·007(1)	−0·0008(5)

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are sent as full-size copies).

The structure shows the alternating sulphur nitrogen chain, NSNSNSN arranged roughly in a horseshoe shape with the diphenylmethylene groups attached to the terminal nitrogens.[16] A comparison of the angles and

TABLE 3

Bond lengths for the structure $[(C_6H_5)_2CNSN]_2S$

Estimated standard deviations are given in parentheses in units of the last significant figure in the parameter itself.

S(1)–N(1)	1·546(6)	C(6)–C(7)	1·417(11)
N(1)–S(2)	1·657(6)	C(7)–C(2)	1·404(10)
S(2)–N(2)	1·679(5)	C(1)–C(8)	1·472(10)
N(2)–C(1)	1·296(9)	C(8)–C(9)	1·391(12)
C(1)–C(2)	1·491(9)	C(9)–C(10)	1·418(13)
C(2)–C(3)	1·408(11)	C(10)–C(11)	1·386(20)
C(3)–C(4)	1·413(11)	C(11)–C(12)	1·387(20)
C(4)–C(5)	1·407(13)	C(12)–C(13)	1·425(13)
C(5)–C(6)	1·401(13)	C(13)–C(8)	1·406(12)
Non-bonded distances			
S(1)–S(2)	2·859(3)	S(2)–S(2^1)	3·222(2)
N(1)–N(2)	2·494(8)	N(1)–N(1^1)	2·733(8)

TABLE 4

Angles for the structure $[(C_6H_5)_2CNSN]_2S$

N(1)–S(1)–N(1′)	124·2(3)°	C(5)–C(6)–C(7)	120·2(8)
S(1)–N(1)–S(2)	126·4(4)	C(6)–C(7)–C(2)	119·3(7)
N(1)–S(2)–N(2)	96·8(3)	C(7)–C(2)–C(3)	121·3(6)
S(2)–N(2)–C(1)	118·6(5)	C(1)–C(8)–C(9)	119·4(7)
N(2)–C(1)–C(2)	117·2(6)	C(1)–C(8)–C(13)	118·8(7)
N(2)–C(1)–C(8)	123·9(6)	C(8)–C(9)–C(10)	119·4(9)
C(2)–C(1)–C(8)	119·0(6)	C(9)–C(10)–C(11)	119·0(11)
C(1)–C(2)–C(3)	119·4(6)	C(10)–C(11)–C(12)	122·0(10)
C(1)–C(2)–C(7)	119·3(6)	C(11)–C(12)–C(13)	119·8(11)
C(2)–C(3)–C(4)	118·5(8)	C(12)–C(13)–C(8)	117·9(9)
C(3)–C(4)–C(5)	121·0(9)	C(13)–C(8)–C(9)	121·8(7)
C(4)–C(5)–C(6)	119·7(8)		

distances with those of 1,5-di(*p*-chlorophenyl)-2,4-diaza-1,3,5-trithiapenta-2,3-diene [14] shows the central five atoms to be in a similar arrangement in both structures. Both structures show the angle at the central sulphur to be 124° while the angles at the other sulphur atoms are considerably less (96·75—100°). The angles at the central sulphur are among the largest observed for the NSN configuration. The angles at nitrogen are similar in both structures. The structures show the bond between the central sulphur and adjacent nitrogens to be considerably shorter (1·539—1·561) than the other sulphur–nitrogen bonds in the compound (1·567—1·662 Å).

This agrees with certain trends that are evident from other published structures of materials with alternating sulphur–nitrogen chains. Sulphur–nitrogen bond lengths in N–S–N bonding situations tend to fall in two ranges which seem to be in some part correlatable with the angle at the sulphur atom whether the material is cyclic or open chain (Table 5).

There are some sulphur–nitrogen structures in which the angles and distances at sulphur do not fit neatly into one or the other situation. $(Cl_5Sb)_2N_2S_2$ with sulphur nitrogen distances of 1·616 and 1·623 Å, has a very small angle at sulphur due to the degree of strain in the four-membered sulphur–nitrogen ring.

$S_5N_5^+AlCl_4^-$ has three relatively large angles at sulphur and relatively shorter bonds from nitrogen to those sulphurs but it also has two other sulphur atoms with relatively smaller angles and the bonds from those sulphurs do not fall in the larger range as in many other structures.

There are three other sulphur–nitrogen materials whose structures do not show sulphur–nitrogen bond lengths and sulphur angles which are consistent with the 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 (1·617,1·604) while the other is in the shorter range (1·546,1·543).[17,18] $(NSF)_4$ shows a relatively large angle at sulphur of 117·7 and alternating sulphur–nitrogen bonds of 1·660 and 1·540 Å.[9]

Thus some argument can be made for the real significance of 0·1 difference between sulphur–nitrogen bond lengths in the structure described here and for the correlation of this difference with the angle at the sulphur atom.

Both $Ph_2CNSNSNSNCPh_2$ and *p*-ClPhSNSNSPh-*p*Cl show the central five members of the sulphur–nitrogen chain (SNSNS) to be coplanar. In the seven-membered

TABLE 5

Sulphur–nitrogen bond lengths and angles at sulphur

Compound	S–N Bond length	Angle at sulphur	Ref.
S_4N_4	1·596—1·634 Å	103—105°	11
$S_4N_4H_4$	1·667—1·682	108	12
$S_5N_5^+AlCl_4^-$	(1·519—1·583)	108·4—110·2	7
	1·453—1·589	117·9—116·8	
$(Cl_5Sb)_2N_2S_2$	1·616, 1·623	84·9	4
$(NSOCl)_3$	1·564	113·0	8
$S_4N_3^+NO_3^-$	1·493—1·582	119·0—118·8	5
p-$ClC_6H_4SNSNSC_6H_4$*p*-Cl	1·593, 1·561	124·1	14
	1·657, 1·662	100, 100	
$Ph_2CNSNSNSNCPh_2$	1·546	124·22	
	1·657	96·75	
$Ph_3PS_3N_4$	1·693, 1·667	109·22	13
	1·693, 1·608	112·67	
	1·522, 1·589	116·2	

[16] E. M. Holt and S. L. Holt, *J.C.S. Chem. Comm.*, 1973, 36.

[17] A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, 1966, **5**, 1767.

[18] H. M. M. Shearer, to be published; A. J. Banister, personal communication.

chain the deviations from planarity are −0·0124 and 0·0147 while the end nitrogens are 0·546 Å from that plane. In the five-membered sulphur nitrogen chain the deviations from planarity range from 0·005 to 0·0244 and the carbons of the *p*-chloro-phenyl group attached to the end sulphurs are 0·2219 and −0·1055 Å from that plane. Thus it seems that the possible increased stability these systems might gain from total planarity and maximum $p\pi$ or $d\pi$ orbital overlap is not the controlling factor here. There seem to be no steric barriers to planarity of these systems beyond the central five members of each system. It would seem that a more meaningful theoretical view of the sulphur to nitrogen bond lengths and the angles at sulphur bonded to two nitrogens might be found in a discussion of sulphur in different orbital hybridizations with somewhat different orbital geometries and giving rise to different bond lengths as a result.

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