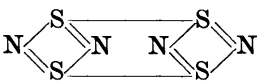
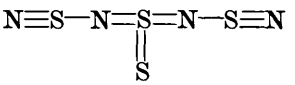
364. *The Formation and Constitution of Sulphur Nitride and So-called Hexasulphamide.*

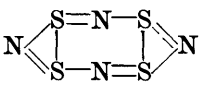
By M. H. M. Arnold, J. A. C. Hugill, and J. M. Hutson.

Sulphur nitride, S_4N_4, is the parent substance of several compounds, but in spite of many investigations, nearly all the constitutions remain obscure. In particular, no structures based on modern valency considerations have been advanced; also, practical details are often scanty or misleading, especially as regards the stability of compounds towards moisture or shock. We have examined the preparation of sulphur nitride and a by-product, the so-called hexasulphamide, and have put forward structures for them.

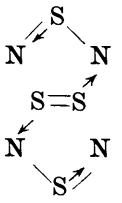
Sulphur Nitride.—This compound is usually known as nitrogen sulphide, but it is formally a nitride, giving ammonia and not hydrogen sulphide on hydrolysis. Its preparation by the action of ammonia on a sulphur chloride is a complicated reaction which throws no light on its structure, for which (I) was proposed by Muthmann and Clever (*Z. anorg. Chem.*, 1896, **13**, 200), and (II) and (III) by Ruff and Geisel (*Ber.*, 1904, **37**, 1573), the last being supported by Meuwsen (*Ber.*, 1929, **62**, 1959). None of these formulations is entirely satisfactory even when modernised, and none accounts satisfactorily for the reactions; moreover, (I) and (III) are stereochemically very improbable. The authors

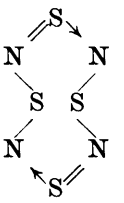

(I.)

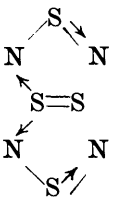

(II.)


(III.)

propose the structure (IV*a*), in resonance with the subsidiary structures (IV*b*) and (IV*c*), the last being a modification of (II). It will be seen that a number of modifications of these structures can exist, all of which play a part in the resonance.


(IV*a*.)


(IV*b*.)


(IV*c*.)

This structure is supported by the following considerations:

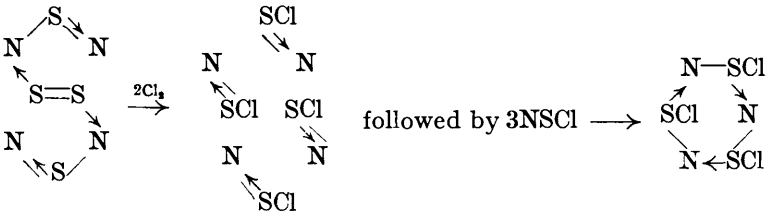
1. Sulphur nitride is hydrolysed quantitatively by cold dilute alkali (the conditions under which rearrangement is least likely to occur):

$$S_4N_4 + 6NaOH + 3H_2O = 4NH_3 + Na_2S_2O_3 + 2Na_2SO_3$$

(Fordos and Gélis, *Compt. rend.*, 1850, **31**, 702; see also Meuwsen, quoted by Jaeger and Zanstra, *Proc. K. Akad. Wetensch. Amsterdam*, 1931, **34**, 782).

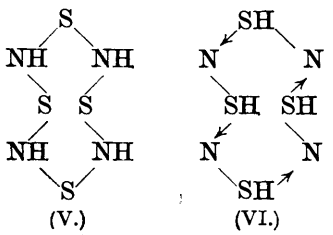
2. On complete reduction, no hydrazine can be detected, indicating that no two nitrogen atoms are joined together (Meuwsen, *loc. cit.*), but we do not regard this argument as conclusive.

3. Chlorine yields a substance which Meuwsen (*Ber.*, 1931, **64**, 2301, 2311) has shown to be $(NSCl)_3$. The reaction can be explained thus :



4. Sulphur nitride forms numerous addition compounds, *e.g.*, S_4N_4,$SnCl_4$ and S_4N_4,$MoCl_4$ (Davis, J., 1905, **87**, 1836), which can best be formulated with a co-ordinate link from the unique sulphur atom of (IV*c*) to the metallic atom.

5. On reduction with alcoholic stannous chloride, sulphur nitride gives $(NSH)_4$, possibly (VI) (Meuwsen, *loc. cit.*, p. 2311). We prefer (V), which shows similarity to the puckered octagonal S_8 ring known to exist in rhombic sulphur (Warren and Burwell, *J. Chem. Physics*, 1935, **3**, 6).



(V.) (VI.)

(These structures are so written to illustrate their derivation from S_4N_4. They will not be planar, but puckered.)

6. With boiling acetyl chloride, sulphur nitride yields thiotrithiazyl chloride, N_3S_4Cl, which, from its chemical properties, is probably a salt, giving the bromide, nitrate, or thiocyanate with the appropriate strong acid (Muthmann and Seitter, *Ber.*, 1897, **30**, 627; Vosnessenski, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1037). We propose the structure (VII) for the thiotrithiazyl ion, and in this connexion the structure (VIII) for sulphur

(VII.) (VIII.)

nitride was considered, as it explains the reaction very simply; further, it is in general agreement with Jaeger and Zanstra's crystal measurements (see below). However, (VIII) does not readily account for the other reactions of sulphur nitride, and is also stereochemically very improbable, as the apical sulphur atom, having no unshared electrons, cannot assume a pyramidal configuration. Moreover, from the stereochemistry of carbon we should expect the double bond to be coplanar with the two co-ordinate links.

7. The crystal structures of sulphur nitride and its tetrahydride have been found by Jaeger and Zanstra (*loc. cit.*) to be exceedingly complicated, the unit cell containing four molecules. For both compounds they deduce structures consisting of distorted interpenetrating tetrahedra of nitrogen and sulphur atoms, similar to (VIII), but the results do not exclude the possibility of other structures agreeing equally well with the observed intensities.

8. Dr. D. Ll. Hammick has pointed out that in all known structures the polarity of the S–N co-ordinate link is S→N, in agreement with all our structures, which were proposed independently of this information. The N–O co-ordinate link, on the other hand, has the opposite polarity, and this may be one explanation why nitric oxide does not polymerise to a compound analogous to S_4N_4.

"*Hexasulphamide.*"—Macbeth and Graham (*Proc. Roy. Irish Acad.*, 1923, **36**, 31) obtained square white plates on concentration of the reaction liquors after removal of sulphur nitride, and assigned to the compound the composition S_6NH_2. Their analyses

and ours agree best with the ratio 6S : N, but the percentage of hydrogen is too small to be determined directly, and as it bears all the errors of the other determinations if determined indirectly, the number of atoms of hydrogen cannot be found by analysis. The molecular weight of our specimens is in reasonably good agreement with $S_{18}N_3H_x$.

Very few reactions give a clue to the constitution, for the compound usually either fails to react or breaks down completely into ammonia, sulphur acids, and free sulphur. The following reactions are typical.

1. With nitrous acid in aqueous-alcoholic solution, some nitrogen is evolved, the residue containing mainly sulphur, sulphide, and sulphate. This may indicate the presence of primary amino-groups.

2. In presence of a trace of alkali, hexasulphamide is readily oxidised by the air or hydrogen peroxide, in alcohol or acetone, to give a vivid blue to purple solution, which is unstable and deposits sulphur on standing for a few hours. The probable constitution of the coloured compound is discussed below.

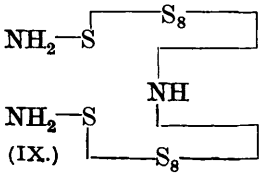
3. Hexasulphamide evolves ammonia on heating (thus proving the presence of hydrogen), leaving a mixture of sulphur and sulphur nitride.

4. It does not react with formaldehyde, benzaldehyde, or acetic anhydride.

5. Attempts to carry out the *iso*nitrile reaction led to oxidation and hydrolysis, ammonia and probably some carbonyl sulphide being evolved.

6. Hexasulphamide reacts with acetyl chloride, but the product has not yet been investigated.

We are unable to advance a convincing structure for hexasulphamide. Its stability in solution and in the fused state shows that it cannot be merely a molecular compound. On the other hand, a chemical formulation necessitates long sulphur chains. We consider that 16 of the sulphur atoms exist as two broken S_8 rings, joined by the group $S_2N_3H_x$. Assuming that the compound is a primary amine, we suggest the structure (IX), $S_{18}N_3H_5$, as a possibility.



(IX.)

Colour Reactions in the Sulphur Nitride Series.—The characteristic colour reactions in this series have been noticed by most investigators, notably Vosnessenski (*loc. cit.*), and appear to be given by most of the compounds, except $(SNH)_4$. The reaction consists in the development of a red to blue colour when the solution is treated with alcoholic alkali; the colours are transient and no solids have been isolated. We investigated the colours formed from sulphur nitride and hexasulphamide, and found them to be due to atmospheric oxidation in presence of alkali. This is shown by the following facts. (1) The rate of formation and the depth attained by the colours is increased by shaking, bubbling air through the solution, or exposing a larger surface area to the air. (2) The maximum colour is developed at once on the addition of alkaline alcoholic hydrogen peroxide. (3) It is inhibited by formaldehyde. (4) Only a small amount of alkali is necessary for the formation of the colours : excess destroys them.

Macbeth and Graham (*loc. cit.*) claim that pure sulphur nitride does not give this colour reaction, but our purest specimens gave a coloration with alkaline alcoholic hydrogen peroxide, and, with difficulty, on aerial oxidation. Certain earlier workers state that sulphur nitride gives the colours if contaminated with sulphur from the reaction mixture. This "sulphur" was probably hexasulphamide. Acetone was more suitable than alcohol for the development of the colours, and also greatly increased their stability. The colours are altered on addition of water or benzene, as shown in the following table.

Substance.	Solvent : Acetone.	Colour on addition of Benzene.	Colour on addition of Water.
S_4N_4	Mauve reflected, magenta transmitted	Yellow	Mauve
$S_{18}N_3H_5$	Blue reflected, dark purple transmitted	Deep blue	Mauve

The product from sulphur nitride was very transient, and in a few minutes the solution became colourless and deposited sulphur. The product from hexasulphamide was much more stable, the colour remaining for some hours even in aqueous solution. It was dis-

charged by strong acid or alkali with separation of sulphur, but was stable up to the b. p. of benzene. Rapid evaporation of an acetone solution gave a yellow solid which rapidly decomposed; if it was redissolved before decomposition occurred, it regenerated the coloured solution.

Nature of the colours. The origin of the colours, their vividness, and the deposition of a yellow solid suggest that they are similar to peroxylaminesulphonic acid, obtained by the oxidation of hydroxylaminedisulphonic acid with alkaline lead peroxide, and having the empirical formula $(SO_3H)_2,NO$. Asmussen (*Z. anorg. Chem.*, 1933, **212**, 317) has shown that the yellow solid salts of this acid are feebly paramagnetic, whereas the deep purple solutions have the strong paramagnetism typical of " odd molecules." They thus probably contain the free radicals $(SO_3H)_2{=}\overset{|}{N}{\rightarrow}O$. It seems likely that similar free radicals are responsible for the oxidation colours in the sulphur nitride series.

Experimental.

Sulphur Nitride.—The usual method of preparation consists in passing ammonia into one of the sulphur chlorides in a suitable inert diluent; *e.g.*, carbon disulphide or tetrachloride, chloroform, benzene, or ether.

Using benzene as diluent for thionyl chloride (Schenck, *Annalen*, 1896, **290**, 171) we failed to obtain a yield, and with sulphur dichloride (Schenck, *loc. cit.*; Ruff and Geisel, *loc. cit.*; Meuwsen, *Ber.*, 1929, **62**, 1959) the yields were bad, being negligible from benzene or carbon tetrachloride, and the bulk of the product being a red tar. We finally found that good clean yields were afforded by a modification of Macbeth and Graham's method (*loc. cit.*). Sulphur monochloride is added to ten times its weight of chloroform and cooled in a freezing mixture; dry ammonia is then passed in with occasional shaking, no precautions being taken to exclude moisture. The first reaction is somewhat violent; pink and brown vapours are given off, and the contents of the flask turn dark brown or black. This colour appears to be due to a pungent, unstable intermediate compound, which can be filtered off, but soon decomposes with formation of sulphur chloride. After the violence has abated, the freezing mixture is removed, and the temperature allowed to rise. (Low temperatures at this stage result in poor yields of sulphur nitride and the formation of large amounts of hexasulphamide.) The stream of ammonia is continued until the reaction mixture changes from a greenish-black to a clear salmon-red colour; the mixture is now filtered from the large bulk of ammonium chloride and concentrated to one-quarter of its volume. Addition of alcohol in excess then precipitates sulphur and sulphur nitride. Concentration of the filtrate yields a little more nitride, and then hexasulphamide; the extreme tail fraction, a red oil with a strong sickly smell, deposits sulphur on standing and probably consists of nitrogen pentasulphide, but has not been examined further. Sulphur nitride was freed from sulphur by extraction with carbon disulphide, and recrystallised from benzene or chloroform. It forms bright orange-yellow needles, darkening to scarlet on heating, m. p. 180° (lit., 178—179°), b. p. *ca.* 185° (Found : N, 30·55; S, 69·88. Calc. for S_4N_4 : N, 30·43; S, 69·57%). It is soluble in organic solvents, but insoluble in and not wetted by water. The solid is quite non-explosive at room temperature, and burns quietly in air; it explodes violently, however, in a m. p. tube at 195° (cf. Burt and Usher, *Proc. Roy. Soc.*, 1911, *A*, **85**, 82; but see also Schenck, *loc. cit.*, who had to keep his sulphur nitride in paper boxes to avoid explosions). It is possible that some of the very explosive specimens obtained by earlier workers were contaminated by nitrogen trichloride, due to too careful drying of the reaction mixture and the use of sulphur dichloride. Although readily oxidised in presence of alkali, sulphur nitride is otherwise stable to air, and can be kept without decomposition. The pure compound is odourless; the specimens obtained by van Valkenburgh and Bailar (*J. Amer. Chem. Soc.*, 1925, **47**, 2134) were probably contaminated with the red oil (see above).

Sulphur nitride was also made with ether as diluent, as recommended by the latter authors. We found no trace of the evil-smelling compounds described by them as being formed on prolonged addition of ammonia. Since the reaction flask has to be kept cold to retain the ether, the yield of sulphur nitride is poor, the bulk of the product being hexasulphamide. The filtrate from the ammonium chloride is best treated by evaporating it to dryness and then taking up the residue with chloroform, from which sulphur nitride can be precipitated with alcohol.

If the reaction (in chloroform) be stopped at the greenish-black stage, the yield is poor and is contaminated by various coloured tars at every stage of the subsequent process.

Hexasulphamide.—Macbeth and Graham (*loc. cit.*) discovered this substance in the sulphur nitride mother-liquors. We concentrated the reaction liquors, after removal of sulphur nitride, to small bulk, and purified the product by repeated crystallisation from alcohol. Hexasulphamide forms very characteristic, creamy, square plates, which grow to large square tabular crystals on slow crystallisation; m. p. 110° (Macbeth and Graham, m. p. 105°) [Found: N, 6·61; S, 91·45; *M*, 592 (slight decomp.). Calc. for $S_{18}N_3H_5$: N, 6·72; S, 92·30; *M*, 624]. It is soluble in organic solvents, especially carbon disulphide, and also in aqueous alcohol and yellow ammonium sulphide. It is insoluble in, unwetted by, and stable towards water, and is odourless, non-explosive, and stable to air except in presence of alkali, but is decomposed by concentrated nitric acid with considerable violence.

We thank Dr. F. M. Brewer for permission to carry out this investigation. Work on this subject is proceeding.

OLD CHEMISTRY DEPARTMENT, UNIVERSITY OF OXFORD. [*Received, May 14th*, 1936.]