

301. The Structure of (SNH)₄ and its Derivatives.

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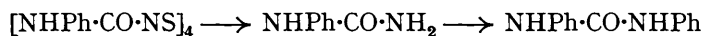
The compound (SNH)₄, formed by reduction of sulphur nitride (S₄N₄), has been shown to have the structure (I; R = H). Compounds of the type (SNR)₄, where R = CH₂·OAc, *p*-CH₂·O·CO·C₆H₄·NO₂, and CO·NHPh, have been prepared, and the compound (SNCH₃O)₄ further investigated.

By the reduction of sulphur nitride, S₄N₄, with alcoholic stannous chloride, Wölbling (*Z. anorg. Chem.*, 1908, **57**, 281) obtained a compound of the composition SNH, which he did not investigate further. Meuwsen (*Ber.*, 1929, **62**, 1959) purified the substance and showed that its molecular weight corresponded to (SNH)₄. There are two probable structures: (I; R = H) and (II), the former of which has been suggested by the author on the basis of his structure for sulphur nitride (Arnold, Hugill, and Hutson, J., 1936,



1645). The equivalence of the four hydrogen atoms is shown by the production of the compound (SNCH₃O)₄ (Meuwsen, *loc. cit.*) with four molecules of formaldehyde. This has now been obtained pure for the first time, and has m. p. 173° (decomp.). Its formulation as an alcohol, (SN·CH₂·OH)₄, follows from the formation of the *tetra-acetate*, m. p. 87·5°, and *tetra-p-nitrobenzoate*, m. p. 222° (decomp.). The two esters show the expected fourfold molecular weight. Reduction with sodium and alcohol does not give methylthiol, showing that there is no carbon-sulphur linkage. The compound can therefore be formulated as (I; R = CH₂·OH) and the parent substance as (I; R = H).

Further evidence for the equivalence of the four hydrogen atoms is furnished by the formation of the quadrimolecular *phenylcarbamylo* derivative, (SN·CO·NHPh)₄, m. p. 224° (decomp.), by the addition to (SNH)₄ of phenyl isocyanate. On hydrolysis with hot hydrochloric acid, this compound yields *s*-diphenylurea, resulting from the action of the hot acid on phenylurea, presumably the primary product:



This reaction shows that the substituent group is attached to nitrogen. The imino-structure is also supported by the fact that (SNH)₄ is soluble only in amyl alcohol (Wölbling, *loc. cit.*), pyridine and piperidine (Meuwsen, *loc. cit.*), and ethyl alcohol. A direct proof of the imino-structure could be obtained by the hydrolysis of an alkyl or acyl derivative, but all attempts to prepare such compounds have failed: there is either gross decomposition or no reaction at all. [The compound (SNET)₄, which appears to have the structure (I; R = Et) (Meuwsen, *Ber.*, 1931, **64**, 2301), as it yields ethylamine on hydrolysis, was prepared by Lengfeld and Stieglitz (*Ber.*, 1895, **28**, 2742) by the action of ethylamine on sulphur dichloride.] An attempt to prepare a more complex derivative of (SNH)₄ by treatment with sulphur monochloride gave a *product*, S₂H₈N₃Cl₃, decomp. 170°, which was apparently a salt; as it could not be purified, it was not further investigated.

Meuwsen (*loc. cit.*, 1931) prefers the structure (II) for (SNH)₄, comparing it with sodium hydrogen sulphite in regard to the reaction with formaldehyde (see Bazlen, *Ber.*, 1927, **60**, 1471):



It is clearly erroneous, however, to compare the reactions of a thiol and of a sulphonic acid, for the sulphur atoms have entirely different electronic configurations; the reaction is more reasonably considered as the normal first stage of that between an aldehyde and a secondary amine.

In order to systematise the nomenclature of this series of compounds, the name "*cyclotetrathioimine*" is proposed for (SNH)₄, from which the names of derivatives can be formed according to the ordinary rules.

EXPERIMENTAL.

cycloTetrathioimine, (SNH)₄.—This compound was prepared according to Meuwsen (*loc. cit.*, 1929), *i.e.*, by reduction of sulphur nitride in benzene by stannous chloride; after being washed free from tin, the product was white (Meuwsen's was brown), and after further washing with water, benzene, and ether, it was pure enough for most purposes. Dissolution in hot pyridine and reprecipitation with excess of benzene gave a yield of 49% (cf. 30%; Meuwsen, *loc. cit.*). The yield is greatly reduced if the sulphur nitride contains sulphur, or if the benzene is replaced by carbon tetrachloride. (SNH)₄ crystallises from acetone in colourless needles, decomp. *ca.* 125° to a yellow powder [Found: S, 67.9; N, 29.55; H, 2.2. Calc. for (SNH)₄: S, 68.1; N, 29.8; H, 2.1%]. Wölbling (*loc. cit.*) reports coloration at 80–100°, m. p. 152° (decomp.); Meuwsen (*loc. cit.*, 1931) obtained a yellow colour at 100°, decomp. at 145°.

Tetrakis-hydroxymethylcycloTetrathioimine, (SN·CH₂·OH)₄.—This was prepared according to Meuwsen (*loc. cit.*, 1931), and was recrystallised from alcohol, forming sheaves of needles, m. p. 173° (decomp.) [Found: C, 15.3; H, 3.8; N, 18.0. Calc. for (CH₂ONS)₄: C, 15.6; H, 3.9; N, 18.2%]. (Meuwsen found that the unpurified compound decomposed below 100°.) Although sparingly soluble in most organic solvents, it can also be recrystallised from ether or acetone.

Acetyl derivative. 1 G. of acetyl chloride and 2 g. of potassium carbonate were added to 0.8 g. of the foregoing compound in ethyl acetate, and the mixture warmed for 15 mins. on the water-bath, a vigorous reaction soon setting in. Inorganic matter was filtered off, ethyl acetate distilled, and the residue twice recrystallised from ether, forming fluffy rosettes (1.1 g., 90%), m. p. 87.5° [Found: C, 30.5; H, 4.3; N, 11.95; *M*, ebullioscopic in ethyl acetate, 460. (C₈H₈O₂NS)₄ requires C, 30.25; H, 4.2; N, 11.8%; *M*, 476].

p-Nitrobenzoyl derivative. 1 G. of (I; R = CH₂·OH), 2.5 g. of *p*-nitrobenzoyl chloride, and 2 ml. of benzene were heated together on the water-bath for 15 mins. The product was washed with hot benzene, dissolved in hot nitrobenzene, and precipitated from the cooled solution by excess of carbon tetrachloride. It was recrystallised from nitrobenzene-acetone, in which it is fairly soluble; creamy, shining plates, m. p. 222° (decomp.) [Found: C, 43.0; H, 3.2; N, 12.5; *M*, cryoscopic in nitrobenzene, 855, 875. (C₈H₆O₄N₂S)₄ requires C, 42.5; H, 2.6; N, 12.4%; *M*, 904], insoluble in all solvents except those mentioned above.

Reaction between (SNH)₄ and Phenyl isoCyanate.—6.7 G. of (I; R = H) and 17 g. of phenyl isocyanate were heated under reflux with 20 ml. of benzene for 4 hours, the mixture cooled, and the residue filtered off, washed with benzene, and recrystallised from acetone; yield, 10 g. (43%) of pale creamy needles, m. p. 224° (decomp.) [Found: N, 16.9, 16.8; *M*, ebullioscopic in acetone, 660, 685. (C₇H₆ON₂S)₄ requires N, 16.7%; *M*, 664], soluble in alcohol and acetone, but only sparingly soluble in carbon tetrachloride and benzene.

Hydrolysis of product. The phenylcarbonyl compound (I; R = NHPh·CO) was dissolved in alcohol, and concentrated hydrochloric acid added to give a 10% solution; when this was boiled, sulphur dioxide was evolved and sulphur precipitated. The solution was filtered hot and neutralised with sodium carbonate, the precipitate being then dried and recrystallised from alcohol, affording colourless needles; m. p., and mixed m. p. with *s*-diphenylurea (m. p. 234°), 234°.

Reaction between (SNH)₄ and Sulphur Monochloride.—Excess of the chloride was added to a suspension of (SNH)₄ in cold carbon tetrachloride. The mixture boiled at once and deposited a precipitate, which was filtered off, washed with carbon tetrachloride, carbon disulphide, and ether, and dried. The product was a pale yellow-brown powder, darkening *ca.* 140°, decomp. 170° [Found: H, 4.2; N, 18.5; S, 30.2; Cl, by diff., 47.1. H₈N₃S₂Cl₃ requires H, 3.7; N, 19.1; S, 29.2; Cl, 48.0%]. It was insoluble in all solvents except water and alcohol, and both these solutions rapidly darkened and deposited a black precipitate, so the compound could not be purified. Its solution in water, before darkening set in, gave silver chloride with silver nitrate, and no colour with ethyl nitrite. Its properties are similar to those of the compound N₃S₄Cl, discovered by Demarçay (*Compt. rend.*, 1880, 91, 1066) and shown by the author (unpublished work) to be a salt. The structure NH(S·NH₂,HCl)₂,HCl is therefore tentatively suggested.