A New Sulphur Nitride with Fused Rings

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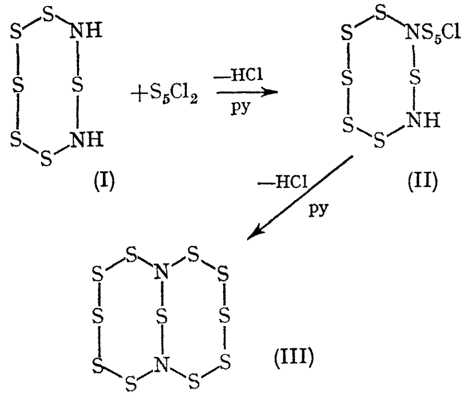
Summary The synthesis of a new sulphur nitride $S_{11}N_2$ is described; its molecule probably consists of two fused eight-membered rings.

SEVEN sulphur imides derived from cyclo-octasulphur by replacement of sulphur atoms with NH groups are known.[1] Their molecules are puckered rings resembling the S_8 ring in shape. Some time ago, when working with a Catalin model of one of these, 1,3-hexasulphur di-imide (I), we found that the two nitrogen "atoms" could be bridged by five additional sulphurs to form a model of the then unknown fused-ring nitride $S_{11}N_2$ (III). Both rings in the model had the same shape as in (I), and all its bond angles and dihedral angles were satisfactory, so it seemed likely that the nitride would be stable. We have now prepared a new nitride of the formula $S_{11}N_2$ which we believe to be (III).



The method of synthesis was a double condensation of S_5Cl_2 with (I): condensations of this kind between chlorosulphanes and sulphur imides have previously been reported,[2] but this is the first example of ring-closure in such a system. At the second (cyclisation) stage there is competition from condensation of the intermediate (II) with a second molecule of (I). To minimise the extent of the competing reaction we used the Ruggli–Ziegler dilution technique; CS_2 solutions of S_5Cl_2,[3] and of (I)[1] plus pyridine, were added over 3 hr. at stoicheiometrically equivalent rates to a large volume of stirred CS_2. The sulphur compounds formed were separated on a chromatographic column of polystyrene gel (Bio Beads S-X8); gel-permeation was adopted because conventional adsorption chromatography will not separate $S_{11}N_2$ from S_8 unavoidably introduced with the starting material S_5Cl_2. The best of three similar preparations from 1 g. of (I) gave 150 mg. of the nitride (9% of theoretical). Elemental analyses for nitrogen and sulphur were in good agreement with the formula $S_{11}N_2$. The heaviest ion found in the mass spectrum was $S_{11}N_2^+$.

The new nitride is readily soluble in CS_2. On slow evaporation of its solution in this solvent, it crystallises in pyramids of a pale amber colour which darken slowly on exposure to light, and melt with decomposition at 150—155°. The only bands in the i.r. spectrum of a CS_2 solution between 650 and 4000 cm.$^{-1}$ are in the S–N stretching region. They are: 766 (strong, narrow, symmetrical); 733 (medium, narrow, symmetrical); and 820 cm.$^{-1}$ (weak, with a shoulder at 810 cm.$^{-1}$). On a thin-layer plate of weakly-active silica gel, the $S_{11}N_2$ travels with $R_F = 1$, like S_8.

We are beginning an *X*-ray crystallographic study of $S_{11}N_2$.

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