# The Crystal Structure of $N_3S_3F_3$

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*Summary* The structure of $N_3S_3F_3$ is a six-membered $(NS)_3$ ring with a chair conformation, the fluorine atoms being in axial positions; in contrast to $N_4S_4F_4$, all S–N bonds are of equal length (1·593 Å) as a result of bond delocalisation.

*X*-RAY structure investigations on halogeno-cyclothiazenes (thiazyl halides) and oxohalogeno-cyclothiazenes show complete bond equalisation in the S–N rings by delocalised $d_\pi$–$p_\pi$ bonding;[1,2] $N_4S_4F_4$, as the only exception of this rule, has alternatingly weak (bond order 1·1) and strong (1·7) S–N ring bonds.[3]

In order to test the hypothesis that the presence of the strongly electronegative substituents was responsible for this unique behaviour, we investigated the structure of trifluorocyclotrithiazene $N_3S_3F_3$ by single crystal *X*-ray methods. The compound has been prepared as colourless crystals from the reaction of $AgF_2$ on $N_3S_3Cl_3$ suspended in $CCl_4$.[4] Because of the appreciable sublimation pressure of $N_3S_3F_3$ at room temperature, the preparation of the crystals and data collection had to be done at $-20$ °C. $N_3S_3F_3$ crystallises in the space group $R\bar{3}$-$C_{3i}$[2] (No. 148) with the hexagonal cell having $a = 10{\cdot}238$, $c = 9{\cdot}535$ Å, $U = 865{\cdot}5$ Å$^3$, $D_c = 2{\cdot}284$ g cm$^{-3}$ (+20 °C), $D_m = 2{\cdot}27$ (+20 °C), $Z = 6$.

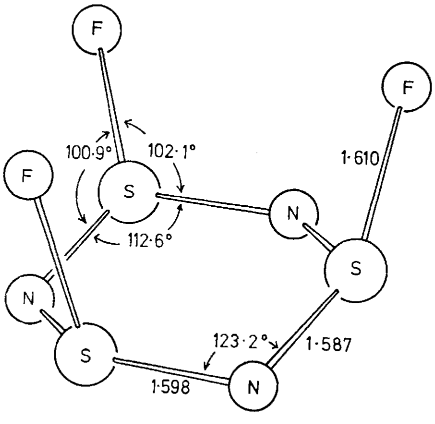

FIGURE *Crystal structure of* $N_3S_3F_3$ *with bond lengths* (Å) *and bond angles*(°).

About 450 unique reflections were measured on a four-circle diffractometer. The structure was solved from the Patterson function and refined by least-squares to an *R* factor of 4·4%.

$N_3S_3F_3$ forms a puckered six-membered ring of alternating S and N atoms with chair conformation, the fluorine atoms being in axial positions. This is in accordance with the n.m.r. spectrum which indicated three equivalent fluorine atoms in the molecule.[5] Bond lengths and bond angles are given in the Figure.

The structure shows that, in contrast to $N_4S_4F_4$, the S–N ring bond lengths in the $N_3S_3F_3$ molecule are *not* alternatingly different. The experimental values for $N_3S_3F_3$ (1·587 and 1·598 Å with standard deviations of 0·003 Å) can be regarded as statistically equal (the difference of 0·011 Å is 2·6 $\sigma$ of the combined error and is only possibly significant). The average of 1·593 Å corresponds to the mean value of the two different bond lengths in $N_4S_4F_4$ (1·540 and 1·660 Å). The estimated S–N bond order in $N_3S_3F_3$ is 1·4.[6] The relatively long S–F bond length in $N_3S_3F_3$ is similar to other S$^{IV}$–F distances in N–S–F compounds.[3,7]

The crystallographic symmetry of the $N_3S_3F_3$ molecule in the solid is $C_3$, but the N–S–F bond angles (see Figure) show that it is very close to $C_{3v}$. The distance between the SSS and NNN planes is 0·23 Å. The intermolecular distances do not indicate any charge transfer interactions as in $N_3S_3Cl_3$. The shortest intermolecular van der Waals contact is 2·925 Å (F · · · F).

The molecular structure of $N_3S_3F_3$ and of trichlorocyclotrithiazene $N_3S_3Cl_3$[2] are similar, in spite of their different crystalline arrangements. The S–N bonds in $N_3S_3F_3$ seem to be slightly shorter than in $N_3S_3Cl_3$ (1·605 at $-100$ °C). Smaller intramolecular F · · · F repulsions result in significantly smaller N–S–Hal bond angles in $N_3S_3F_3$ as compared with $N_3S_3Cl_3$ (113·7°).

The structure determination shows that in the puckered $(SN)_x$ rings, as in corresponding (essentially planar) phosphazene ring systems, the tendency towards complete bond equalisation through delocalised $d_\pi$–$p_\pi$ bonds[8] is a general one, also in compounds with fluorine substituents. If this delocalisation is incomplete, as in $N_4S_4F_4$, steric reasosn rather than electronegativity influences must be responsible. The strong repulsions of the equatorial sulphur lone pairs force the $N_4S_4F_4$ molecule into a conformation which favours $d_\pi$–$p_\pi$ overlap only with one of the two N neighbours.

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