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The Structures of Sulfur-Nitrogen Compounds

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Abstract

The structures and bonding of the following species are discussed:
 S_2N_2 , $S_2N_2^+$, $S_2N_2^{2+}$, $S_3N_3Cl_3$, $S_3N_3O_3Cl_3$, S_7NH , $S_6(NH)_2$, $S_5(NH)_3$, $S_4N_4H_4$,
 $S_4N_4F_4$, $S_4N_4^{2-}$, S_4N_4 , $S_4N_4^{2+}$, $S_5N_5^+$, $S_3N_2O_2$, $S_3N_2Cl^+$, $S_3N_3NPPH_3$, S_4N_2 ,
and $S_4N_3^+$. These species are characterized by rings or chains of alternating sulfur and nitrogen atoms. The structures can be rationalized by comparison with isoelectronic compounds of known structure and by the assumption of delocalized $p\pi$ bonding whenever possible.

Introduction

In this paper I shall discuss the structures of compounds which contain rings or chains of alternating sulfur and nitrogen atoms. During the last 15 years or so this class of compounds has been a source of frustration and mystery to chemists because various structure determinations have often showed that structures which had been predicted for these compounds were wrong. However, enough structures of such compounds are now known that it is possible to systematize and rationalize the data. I shall discuss this rationale and use it to make several predictions.

The structural rationale is based in part on the comparison of sulfur-nitrogen compounds with isoelectronic compounds of known structure and on the assumption of delocalized $p\pi$ bonding whenever possible. In the study of these structures, it became apparent that certain empirical bonding rules must be kept in mind; these are discussed in the following section.

Empirical Bonding Rules

Rule 1. Bond angles at sulfur atoms are usually in the neighborhood of 100° . This rule is not peculiar to sulfur-nitrogen compounds. For other examples we may cite the Cl-S-Cl angle of 100.3° in SCl_2 and the F-S-F and O-S-F angles of 92.8 and 106.8° , respectively, in SOF_2 . (1) The rule is undoubtedly a consequence of the tendency for sulfur atoms to use mainly orthogonal p orbitals in bonding.

Rule 2. Tervalent sulfur atoms (i.e., sulfur atoms bonded to three other atoms) cannot engage in $p\pi$ - $p\pi$ bonding. This rule seems reasonable

in view of Rule 1. The lone pair of a tervalent sulfur atom is essentially in a 3s orbital, and extensive hybridization would be required for it to be used in π bonding.

Rule 3. Bond angles at divalent nitrogen atoms which are involved in π bonding are usually 120° or greater. The larger bond angles at nitrogen atoms are probably a consequence of the smaller size of nitrogen atoms and the greater repulsion between valence-shell electron pairs.

Rule 4. In cyclic $(\text{SN})_x$ systems, the Hückel $4n + 2$ Rule is applicable. That is, a planar structure with delocalized π bonding is favored when n, the number of π electrons, is 2, 6, 10 or 14. (2) In noncyclic chain systems, π bonding is considerably more localized.

Rule 5. Lone pair-lone pair repulsion between directly attached atoms is structurally unimportant; however it can be significant between other atoms which are close together because of the molecular geometry.

$(\text{SN})_x$ Ring Systems

The simplest known $(\text{SN})_x$ ring system is found in the compound S_2N_2 . This molecule and its isoelectronic analog, S_4^{2+} , have square planar configurations (3-5). Because the ring has 6 π electrons, the $4n + 2$ Rule is obeyed and the planar structure is stable. According to simple Hückel molecular orbital theory, the molecule has one pair of bonding π electrons, in agreement with valence bond theory:

Although the free radical $S_2N_2^+$ has been identified, the only available structural information is that the two nitrogen atoms are structurally equivalent and that the two sulfur atoms are structurally equivalent. (6) The species is probably planar (or nearly planar), with the odd electron occupying a nonbonding π orbital.

The species $S_2N_2^{2+}$ is at present unknown. On the basis of its analogy to the P_4 molecule, one might predict a tetrahedral structure; however in view of the tendency for bond angles at nitrogen atoms to be larger than those at second-row atoms, the acute bond angles in the tetrahedral structure may introduce so much instability as to make an oblong or rhomboidal planar structure, with two localized double bonds, stable:

A six-membered $(SN)_3$ ring is found in the molecule $S_3N_3Cl_3$, illustrated in Figure 1 and in the following valence-bond structure.

The tervalent sulfur atoms prohibit π bonding, and the ring has a non-planar conformation, analogous to the chair conformation of cyclohexane.

(7) However, the ring is nearly planar (the average distance of the nitrogen atoms from the plane of the sulfur atoms is only 0.2 Å) and the $S-N$ bond distance (1.605 Å) is significantly shorter than the S-N

distance in $S_4N_4H_4$ (1.65 Å). Although these features suggest that $d\pi-p\pi$ bonding exists in the ring, it should be pointed out that the short $^+S-N^-$ bond distance may be simply a consequence of the polarity of the bond. The molecule is remarkable because all three chlorine atoms occupy apical, rather than equatorial, positions and because the nonbonding electron orbitals of each of the six pairs of adjacent sulfur and nitrogen atoms are essentially coplanar. One might have predicted that the chlorines would occupy equatorial positions so that the nonbonding orbitals on adjacent atoms would be forced to lie in different planes. However, such a structure would cause the nonbonding electrons of the chlorine atoms to interact with those of the nitrogen atoms. Apparently the latter interaction is more repulsive than that between nonbonding electrons on adjacent ring atoms. This observation will be useful later in our interpretation of the structure of $S_4N_4F_4$.

The structure of $S_3N_3O_3Cl_3$ is essentially the same as that of $S_3N_3Cl_3$ except that oxygen atoms occupy the positions of the sulfur lone pairs.

(8) It is interesting that, in the isoelectronic compound $P_3N_3Cl_6$, the P_3N_3 ring is almost exactly planar. This near planarity may be caused by $d\pi-p\pi$ bonding and is probably favored in the P_3N_3 ring more than in the S_3N_3 ring because of the greater size of the phosphorus atom and the consequent relative ease of achieving an N-P-N bond angle near 120° .

The S_8 ring, if planar, would have 16 π electrons and consequently an equal number of antibonding and bonding π electrons. Thus the nonplanar crown configuration, with bond angles of 108° , is stable. The sulfur imides correspond to S_8 rings in which 1, 2, 3, or 4 of the sulfur atoms

have been replaced with the isoelectronic NH groups - with the restriction that the NH groups never occupy adjacent positions in the ring. Thus, as far as is known, S_7NH , $S_5N_3H_3$, $S_4N_4H_4$, and the isomers of $S_6N_2H_2$ have structures completely analogous to that of S_8 . (9)

In $S_4N_4F_4$, the fluorine atoms are attached to the sulfur atoms; consequently the $(SN)_4$ ring has no π bonding and is highly puckered, as shown in Figure 2. (10,11) The remarkable feature of this structure is that there are two S-N bond distances (1.66 and 1.54 Å) which occur alternately in the ring. In Fig. 2, the S_1-N_1 distance is 1.66 Å and the N_1-S_2 distance is 1.54 Å. By examination of Fig. 2, it can be seen that the S_1-N_1 and N_1-S_2 bonds are stereochemically quite different. The S_1-N_1 bond is longer probably because of repulsive interaction of the nonbonding electrons of fluorine atom F_1 with the nonbonding electrons of nitrogen atom N_1 . The N_1-S_2 bond is shorter probably because there is no such interaction between the nonbonding electrons of atoms F_2 and N_1 . It is significant to note that, if atoms F_1 and F_3 were flipped to the upper side of the ring, there would be no resultant net advantage in terms of nonbonding electron interactions. In such a conformation, the S-N bonds would be expected to occur in the sequence s,s,l,l,s,s,l,l (s = short; l = long).

The Se_8^{2+} ion has the remarkable structure illustrated in Fig. 3. (12) Although a planar monocyclic structure with 14 π electrons would fit the $4n + 2$ Rule, such a structure is ruled out by the requirement that the selenium bond angles be in the neighborhood of 95° . Indeed the only conceivable planar structure even with bond angles as high as 105°

is the following, in which two of the atoms are almost on top of each other.

The observed structure of Fig. 3 is derivable from the normal crown conformation of Se_8 by the loss of two electrons, the transannular bridging from $\text{Se}(4)$ to $\text{Se}(5)$, and the ring flip of $\text{Se}(1)$. The species $\text{S}_4\text{N}_4^{2-}$, which is isoelectronic with Se_8^{2+} , has never been unequivocally identified. (13,14) The prediction of its structure is difficult. It might have a structure analogous to that of Se_8^{2+} , or it might have a planar π -bonded structure. A planar structure would not be unreasonable for $\text{S}_4\text{N}_4^{2-}$ because of the ability of nitrogen atoms to have bond angles as high as 153° . (15,16)

Removal of two electrons from Se_8^{2+} to form the hypothetical Se_8^{4+} would be expected to cause the flipping up of $\text{Se}(8)$ and the formation of a bridge from $\text{Se}(8)$ to $\text{Se}(1)$. This cage structure would be analogous to that of the isoelectronic molecule, S_4N_4 , illustrated in Fig. 4. (17)

Removal of two electrons from S_4N_4 would yield the species $\text{S}_4\text{N}_4^{2+}$, which as yet has not been identified but which may be the stable sulfur-nitrogen cationic species which forms when S_4N_4 is dissolved in anhydrous sulfuric acid. (18) This species would be isoelectronic with the cyclo-octatetraenide ion $\text{C}_8\text{H}_8^{2-}$ and, because of adherence to the $4n + 2$ Rule, would be expected to be a planar eight-membered ring of alternating sulfur and nitrogen atoms.

The $S_5N_5^+$ cation is a planar heart-shaped ring of alternating sulfur and nitrogen atoms: (19)

It will be noted that this ten-atom system has 14 π electrons, for which one predicts three π bonds.

Planar Sulfur-Nitrogen Chains

In this section we shall discuss chains of alternating sulfur and nitrogen atoms which are engaged in π bonding but which are not pseudo-aromatic either because of an open chain structure or, in the case of cyclic compounds, because of the presence of ring atoms which block π bonding.

The $S_3N_2O_2$ molecule is a planar chain of sulfur and nitrogen atoms terminated by oxygen atoms: (20)

The indicated structure probably is the principal contributor to the resonance hybrid because it minimizes the separation of positive and negative formal charges and puts negative formal charges on the most

electronegative atoms. As expected, the S_2 -N distance (1.58 Å) is shorter than the S_1 -N distance (1.69 Å).

The $S_3N_2Cl^+$ cation, pictured in Fig. 5, has an essentially planar S_3N_2 ring. (21) Because of the inability of the tervalent sulfur atom to engage in π bonding, π bonding is restricted to the SNSN chain which is attached to the SCl group. Apparently the fact that the tervalent sulfur atom is coplanar with the SNSN chain is accidental. It will be noted that the bond angles in the ion are all normal. From the observed bond distances, we conclude that the π bond is largely localized as indicated in the following structure.

This structure would be expected to be the principal contributor to the resonance hybrid because it involves the least separation of negative and positive formal charges.

The structure of $S_3N_3NPPH_3$ is shown in Fig. 6. (22) Because the tervalent sulfur atom cannot engage in π bonding, the π bonding is restricted to the remaining NSNSN chain of atoms which are coplanar. It is not possible to form a completely planar six membered $(SN)_3$ ring with normal bond angles. However, by allowing the tervalent sulfur atom to flip out of the plane, the other five atoms can maintain planarity with normal bond angles at all six atoms. Because the π orbitals of the nitrogen atoms bonded to the tervalent sulfur atom are not ideally

oriented the π bonding would be expected to be strongest in the bonds to the middle nitrogen atom of the planar NSNSN chain.

The structure of S_4N_2 has not yet been determined. (23) One reasonable possibility is a structure like that of $S_3N_2Cl^+$, in which the chlorine atom has been replaced by a sulfur atom. Another possibility is the six-membered ring structure indicated below.

One would expect that π bonding would be restricted to the SNSNS chain of atoms and that these would be coplanar, with the middle sulfur atom of the SSS chain flipped out of the plane to allow normal bond angles at all the atoms.

The $S_4N_3^+$ ion is a planar seven-membered ring, as shown below. (15,16)

The fact that the S-N bond distances are equal within experimental error indicates that there is considerable delocalization of the π bonding in this ring (except in the S-S bond). The indicated structure would be expected to be the main contributor to the resonance hybrid because it involves the least separation of negative and positive formal charges.

The electronic absorption spectrum of the $S_4N_3^+$ cation has been interpreted in terms of a $\pi \rightarrow \pi^*$ transition. (24,25)

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Figure Captions

- Figure 1. The $S_3N_3Cl_3$ molecule. Reprinted with permission from reference (7).
- Figure 2. The $S_4N_4F_4$ molecule. Reprinted with permission from reference (10).
- Figure 3. The Se_8^{2+} ion. Reprinted with permission from reference (12).
- Figure 4. The S_4N_4 molecule. Reprinted with permission from Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," 2nd ed., Interscience Publishers, New York, 1966.
- Figure 5. The $S_3N_2Cl^+$ ion. Reprinted with permission from reference (21).
- Figure 6. The $S_3N_3NPh_3$ molecule. Reprinted with permission from reference (22).

XBL 712-303

Fig. 1

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Fig. 2

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Fig. 4

XBL 712-307

Fig. 5

XBL 712-304

Fig. 6

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