The Structure of Thiodithiazyl Derivatives
An Example of an Electron-Rich-Four-Center-Bond

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Z. Naturforsch. 35b, 1166-1170 (1980); received April 11, 1980

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Experimental and computational evidence indicates that the five-membered ring system $S_3N_2^+$ has an $^2A_2$ ground state. Different possibilities for the stabilization of $S_3N_2^+$ are discussed on the basis of MO arguments and calculations using semiempirical and ab initio (STO 3G) methods. The theory allows the rationalization of the structures of $S_3N_2Cl_2$, $S_3N_2X$ and $[S_6N_1I]_2^+$. The bonding between the two $S_3N_2^+$ moieties in $[S_4N_4]^2+$ is described as an electron rich six electron four center bond.

Recently the structure of several cyclothiodiazenes has been characterized by X-ray diffraction [1]. As an example we display in Fig. 1 some of the data obtained for $S_3N_2NP_3N_3F_5$ [1], $[S_3N_2Cl]Cl$ [2], $(S_3N_2)_(2)(S_2O_6Cl)_2$ [3] and $(S_3N_2)_(2)(S_2O_6CF)_2$ [4]. In this paper we try to explain the structures of $[S_3N_2Cl]^+$ (1), related species and of $[S_3N_2]_2^+$ (2) in terms of simple perturbation theory aided by molecular orbital (MO) calculations. A similar approach has been used by us to understand $S_4N_4$ [5], $S_4N_2^+$ [6] and some bicyclic sulfur compounds [7].

![Fig. 1. Bond lengths of thiodithiazyl derivatives.](image)

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We start our discussion by considering the planar, neutral $S_3N_2$ ring system belonging to point group $C_2v$ as shown in Fig. 2. In a localized picture we can describe the five-membered ring as consisting of five SN α-bonds connecting the centers and five “lone-pairs”. This makes up for 20 valence electrons and leaves 8 for the π system (see Fig. 2). From the qualitative HMO pattern shown in Fig. 2 and Hunds rule it is likely that $S_3N_2$ has a triplet ground state and thus is unstable under normal conditions. (The five-membered ring of $S_3N_2$ belongs to point group $C_2v$ and therefore all levels are non-degenerate. The energy difference between 1$a_2$ and 2$b_1$ and between 2$a_2$ and 3$b_2$, however, is very small). A stable singlet ground state may be achieved by removing or adding two electrons to $S_3N_2$. Both systems, the dication and the dianion should have a closed shell structure and satisfy Hückels rule for aromatic (6

![Fig. 2. Qualitative MO scheme of $S_3N_2$. For the numbering of the levels only the valence orbitals were considered.](image)
and 10 π) systems. The generation of the dianion seems less favoured since both antibonding π-
molecular orbitals of the five-membered ring system are occupied and thus the system may escape this
unfavourable situation by opening the ring.

X-ray investigations have solved the structure of a radical species which has been obtained from
S4N4 by reaction with acids like H2SO4, SbF5 and AsF3 [8]. It is the radical cation of S3N2. Several
workers reported a five line ESR spectrum [8-10] with a coupling constant of 3.21 G and a g-value of
2.011. This result establishes two equivalent nitrogen atoms. The analysis of the 33S satellites
in the ESR spectrum yields a 33S coupling constant of 8.9 G [10] and indicates two equivalent sulfur
atoms.

In view of the relatively small energy gap be-
tween the orbitals 2a2 and 3b1, the question is raised whether 2a2 or 3b1 correspond to the HOMO
of S3N2+, i.e. whether the ground state is 2A2 or 2B1. An open shell version [11] of the MNDO method [12]
predicts 2a2 for the HOMO and 3b1 for the LUMO

![Fig. 3. AO coefficients of 2a2 and 3b1 of S3N2 as derived from an MNDO calculation.](image)

of S3N2+ as shown in Fig. 2. In Fig. 3 we have shown
the predicted π spin population of 2a2 and 3b1 obtained by the MNDO (open shell) method. A
calculation using the extended Hückel method [13]
provides very similar wave functions. From the
MO coefficients Cμ the electron density ρμ can be calculated and thus the coupling constants
can be estimated in a first order approximation using the McConnell equation (aμ = Qμ · ρμ) [14]
with the parameters QS = 30 G [15] and QN = 25 G [16]. In our case the following coupling constants are derived:

- 2a2 as HOMO: aN = 4 Gauss and aS = 9 Gauss;
- 3b1 as HOMO: aN = 5 Gauss and aS = 0.7 Gauss.

These values are in good agreement with the ESR experiments only if 2a2 is assumed to be the HOMO,
i.e. the ground state of S3N2+ is 2A2.

The unpaired electron in the 2A2 state in S3N2+
is distributed over four centers only and thus a
dimerization or recombination with another radical seems likely. The structure of the chloride 1 can be
looked at as a combination of S2N2+ with a chlorine radical. As a consequence of this view the remaining
6 π-electrons house in the three lowest π-orbitals derived from a linear combination of the p atoms orbitals
of the four remaining centers. The six π electrons are to be placed in the three π-orbitals ψ1 to ψ3

![Fig. 4. Schematic representation of the π-MO's of 1 (a). Overlap populations and net charges of 1 according to a CNDO/2 calculation [17] (b). (The values for the overlap populations were taken from Fig. III of ref. [17]).](image)

(Fig. 4a) which are closely related to those of the corresponding butadiene π-system. In butadiene
only ψ1 and ψ2 are occupied, resulting in a strengthening of bonds 1-2 and 3-4 (double bond character)
while the π-bond order of bond 2-3 is relatively small (single bond character). The additional occu-
pation of ψ3, however, leads to a strengthening of bond 2-3 and a slight weakening of bonds 1-2 and
3-4. A similar conclusion is reached by considering the most likely valence bond structures of 1 [8].

These qualitative arguments agree with the experimental distances (see Fig. 1) found for 1 and are substantiated by the computed net charges and overlap populations obtained by the CNDO/2 meth-
od (see Fig. 4b) [17]. Closely related to the structure of 1 are compounds in which the chlorine atom is
replaced by an atom or group which bears formally a negative charge like O- or N-R. An example of the latter is shown in Figure 1. The alternation of bond lengths found for the latter parallels the
one in 1 as anticipated.

At this point the question should be raised why the recombination is not taking place at the sulfur
center between the nitrogens yielding a more symmetric species \( S_2N_2X \). This can be explained in a qualitative way by considering the HOMO of \( S_2N_2^+ \). As shown in Fig. 2 the HOMO of \( S_2N_2^+ \) belongs to the irreducible representation \( \Lambda_2 \) and thus has a node through the sulfur center between the nitrogen atoms. Using perturbation theory as a guide \[18\] the interaction between the HOMO of \( S_2N_2^+ \) and the HOMO of a radical say \( \text{Cl}^ - \) is most efficient if the chlorine radical attacks at the sulfur positions with nonzero coefficients in the HOMO. Below we compare the total energies for two possible isomers of \( S_2N_2Cl^+ \) using the MNDO method \[12\]. The results are in agreement with our qualitative argumentation.

**Total energy (MNDO) (eV)**

\[
\begin{array}{c}
\text{\( S_2N_2^+ \)} \\
-1470.6 \\
\text{\( S_2N_4^{2+} \)} \\
-1468.7
\end{array}
\]

**The Structure of \( S_2N_4^{2+} \)**

If the radical \( S_2N_2^+ \) finds no partner (e.g. \( \text{Cl}^ -, \text{O}^-, \text{NR}^2 \)) to interact with, a stabilization via dimerization seems likely. Important for our understanding of \( S_2N_4^{2+} \) is the result that the value of the \( 3p_\sigma-3p_\sigma \) overlap integral of the sulfur \( 3p \) orbitals is considerably larger at distances between 4 and 2.5 Å than the overlap integral for the \( 2p_\sigma-2p_\sigma \) interaction of nitrogen \( 2p \) orbitals \[5\]. As a corollary of this result we expect the dimerization to occur via the sulfur centers. Possible structures for dimers are:

![Possible structures for dimers](image)

From the discussion in the preceding chapter the dimerization leading to 4 seems not very likely due to the nodal properties of the HOMO of both \( S_2N_2^+ \) fragments. Furthermore the cases 4 and 5 are disfavoured due to the fact that adjacent sulfur atoms are charged. If our simple model is correct structure 2' and its syn isomer 3 can be looked at as indicated in the drawings: Four \( \pi \)-electrons of each \( S_2N_2^+ \) moiety are formally localized in the NSN-unit, three \( \pi \)-electrons of each \( S_2N_2^+ \) fragment are part of an electron rich four center bond. This picture contrasts that given by Banister *et al.* who proposed that “two aromatic 1,2-dithiolium cations are linked via pairs of sulfur atoms in a four centre 2 electron bond” \[3\]. The model proposed here assumes 4 \( \pi \)-electrons in the NSN-unit, an arrangement which is quite often encountered in sulfurdiimides. The electron rich four center bond, however, is unique and on a first glimpse not at all favourable. To elaborate on this new type of bonding let us first consider the four molecular orbitals which arise from the four \( 3p_\sigma \) atomic orbitals on the sulfur centers of two \( \text{H}_2S_2^+ \) radicals in the arrangement shown in 6.

![Possible structures for dimers](image)

Our model species belongs to point group \( C_{2h} \) and the four linear combinations transform according to \( a_g, b_u, a_u \) and \( b_g \) as shown below.

![Linear combinations](image)

In our model dication 6 three (\( a_g, b_u, a_u \)) of these MO's are occupied, one (\( b_g \)) will be empty. By narrowing \( R \), the distance between the two \( \text{H}_2S_2^+ \) units, the bonding orbitals are expected to be lowered in energy while the antibonding ones are expected to raise. A minimum might emerge if the lowering of \( a_g \) and \( a_u \) outbalances at large distances the raise of \( b_u \). We proceed further by carrying out *ab initio* calculations (STO 3 G) \[19\] on 6 by varying \( R \) only, preserving \( C_{2h} \) symmetry. In Fig. 5 we have plotted the energies of the four MO's \( a_g, b_u, a_u \) and \( b_g \) as well as the total energy of 6 as a function of \( R \). At large values of \( R (> 4 \text{ Å}) \) the MO's are similar.
to those of two isolated $\text{H}_2\text{S}_2^+$ units. The two orbitals of $\pi$-type ($a_g$, $b_u$) and those of $\pi^*$ type ($a_u$, $b_g$) are close in energy as anticipated. By reducing the distance $R$ between the two moieties both the $a_g$ and $a_u$ levels will be stabilized while the $b_u$ and $b_g$ orbitals will be strongly destabilized. It is interesting to note the positive slope of $a_g$ and $a_u$ is larger up to 3 Å than the negative slope of the antibonding combinations. Thus the total energy is lowered since nuclear-nuclear repulsion is still small at these distances.

It should be noted that while the stabilization of the bonding levels $a_g$ and $a_u$ is operative already for relatively long distances, the destabilization of the antibonding levels $b_u$ and $b_g$ is only significant for distances below ca. 3 Å. This behavior is particularly marked for $a_u$ and $b_u$ and is due to interaction of the localized orbitals indicated above with $\sigma^*$ orbitals of the same symmetry. This admixture tends to reduce the antibonding and increase the bonding character, as illustrated in the case of $a_u$ and $b_u$, respectively. A similar but less pronounced mixing is found for $a_g$ and $b_g$.

In case of 2 and 3 an additional stabilization of the electron rich four center bond is found. This stabilization is due to the interaction of the occupied $a_g$ combination of the four center system with the corresponding empty $\pi^*$-combination localized at the NSN fragment. The wave function for the occupied $a_g$ orbital for 2 is shown schematically below.

To obtain an estimate of the energy difference between 2 and 3 we carried out model calculations. For these calculations we assumed the same geometry for each five-membered ring unit as reported for 2 [4]. The planes of the two $\text{S}_3\text{N}_2$ units, however, were taken to be perpendicular to the plane spanned by the four S centers. The total energies obtained by an $ab$ initio calculation (STO 3 G) for the structures closely related to 2, 2' and 3 are:

2': $-2573.1266$ a.u. 3: $-2573.1152$ a.u.

The energy difference between both assumed structures (0.31 eV) is mainly due to the smaller nuclear-nuclear repulsion present in 2'. By adopting the experimental geometry for 2 the total energy found is: $-2573.1415$ a.u. This value is still lower by 0.41 eV than the one found for structure 2'. In Figure 6a the calculated net charges and Mulliken overlap populations [20] for 2 are shown.

This diagram confirms our qualitative picture: the positive charge is mainly localized on the sulfur centers attached to two nitrogen atoms. The $p_z$
Fig. 6. a) Calculated reduced Mulliken overlap populations (left) and net charges (right) for 2. b) Calculated Mulliken gross $p_z$ charges for 2.

gross orbital charges [20] (Figure 6b) show 3.64 $\alpha$-electrons localized on one NSN unit and 5.86 $\pi$-electrons housing in the electron rich four center bond.

The reduced Mulliken overlap populations shown in Figure 6 parallel the X-ray data in so far as the overlap population between the sulfur atoms connecting both moieties is found to be very small. The main contribution comes from the $3p_\alpha-3p_\alpha$ overlap. The calculated value for the $3p_\alpha-3p_\alpha$ overlap population amounts to 0.014.

Our picture of the electron rich six electron four center bond in $[S_3N_2]^{2+}$ is related to the experimentally and theoretically [21] well known inter- or intramolecular three electron S-S bond as established by ESR, optical spectroscopy and CI-mass spectroscopy [22]. This type of bond shown schematically in 7, when extended to radical cations of oxidized 1,2-dithia-compounds (8) is exactly what we describe for $[S_3N_2]^{2+}$, i.e. a six electron four center bond. It might therefore be possible to find experimental evidence for this type of interaction in other 1,2-disulfides.

We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the BASF Ludwigshafen for financial support. We thank Prof. Dr. F. Gerson for helpful discussions and Dr. T. Clark for technical assistance with some of the calculations.

[8] R. J. Gillespie, P. R. Ireland and J. E. Vekris, Canad. J. Chem. 53, 3147 (1975). The distance between the $S_3N_2$ rings is found to be 3.9 Å and thus the reported structure is analogous to that of ref. [3] and [4] (private communication by R. J. Gillespie).