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The Structures of $S_4N_5^{\ominus}$, $S_4N_5^{\oplus}$, and S_5N_6. A Rationalization Based Upon Molecular Orbital Theory

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Using qualitative arguments from molecular orbital theory the essential features of the structures of $S_4N_5^{\ominus}$, $S_4N_5^{\oplus}$, and S_5N_6 can be rationalized. Possible degenerate rearrangements of all three species are discussed. An extension of the presented model allows also the understanding of the structures of As_4S_5 and β-P_4S_5.

Die Strukturen von $S_4N_5^{\ominus}$, $S_4N_5^{\oplus}$ und S_5N_6. Eine Erklärung mit Hilfe der Molekül-Orbital-Theorie

Mit Hilfe qualitativer Argumente aus der Molekül-Orbital-Theorie können die wesentlichen Merkmale der Strukturen von $S_4N_5^{\ominus}$, $S_4N_5^{\oplus}$ und S_5N_6 erklärt werden. Mögliche entartete Umlagerungen aller drei Strukturen werden diskutiert. Eine Erweiterung des vorgeschlagenen Modells erklärt die Strukturen von As_4S_5 und β-P_4S_5.

Recently three compounds with cage like structures containing N and S atoms only, have been prepared: $S_4N_5^{\ominus}$ (**1**)[1], $S_4N_5^{\oplus}$ (**2**)[2], and S_5N_6 (**3**)[3]. Formally all of them can be derived from S_4N_4 by replacing one transannular S – S bond by a nitrogen atom or a NSN fragment (see (1)). The most striking structural difference between **1** and **2** is the $S_3 - S_7$ distance (see Figure 1) which is found to be 2.73 Å in **1** and 4.01 Å in **2**. For **3** again a relatively short $S_3 - S_7$ distance is reported (2.42 Å).

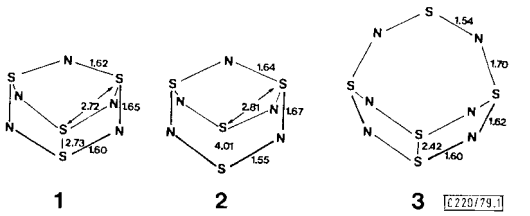

Fig. 1. Bond distances in $S_4N_5^{\ominus}$ (**1**), $S_4N_5^{\oplus}$ (**2**) and S_5N_6 (**3**)

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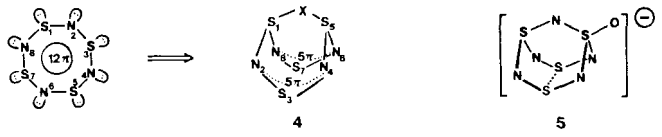
In this paper we rationalize these structures and related ones by using arguments derived from molecular orbital (MO) theory, in analogy to previous examples where we explained the structures of S_4N_4[4] and $S_5N_5^{\oplus}$[5].

We start our discussion with S_4N_4. Assuming a planar structure for this species and considering for each center a "lone pair" and two σ electrons, we are left with 12 valence electrons for the π-system[4] (see below). In this case each sulfur center provides formally two pπ electrons and each nitrogen center one.



Taking one pπ electron on two opposite sulfur centers, say S_1 and S_5, to form σ-bonds with a bridging atom X, leaves 10π electrons in model **4** for the two allylic moieties ($N_2-S_3-N_4$ and $N_6-S_7-N_8$). In Figure 2 the orbital energies of the π MO's of **4** are shown for a model in which X is replaced by two hydrogen atoms for a S_3-S_7 distance of 2.7 and 4.0 Å.

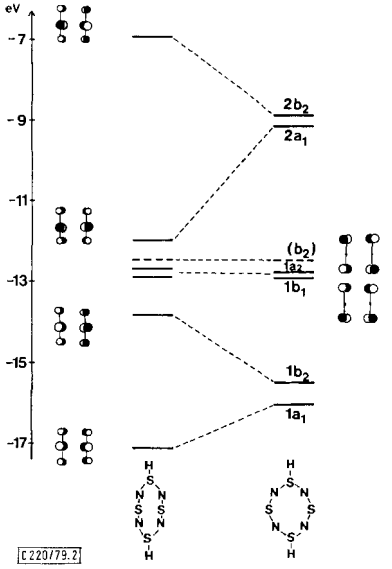


Fig. 2. π-Molecular orbital energies of model **4** according to an extended Hückel calculation for S_3-S_7 = 2.7 Å (left) and 4.0 Å (right)

The anticipated outcome of this correlation diagram is that for large S_3-S_7 distances (Figure 2 right) the energy niveaus are those of two separated allylic π-systems. The relative energies of the niveaus were taken from an extended Hückel (EH)[6] calculation. For small S_3-S_7 distances (see Figure 2 left), however, a considerable interaction is predicted between those MO's belonging to the irreducible representations A_1 and B_2.

The a_1 orbitals will be lowered in energy and the b_2 orbitals will be raised, compared to a system in which the allylic parts are far removed from each other.

Replacing in our model the two hydrogen atoms by a nitrogen bridge as in **1** or **2**, we have to add the $2p\pi$ orbital on nitrogen which belongs to the irreducible representation B_2. For reasons of overlap and energy difference of the basis orbitals its interaction with the other orbitals of the same symmetry can be neglected. The corresponding energy niveau is indicated in Figure 2 by a broken bar. Having constructed the π-molecular orbital schemes for **1** and **2** using an independant electron model we have to fill in the electrons. For **1** the nitrogen bridge contributes formally two electrons, for **2** formally zero. Thus in our π-molecular orbital scheme of Figure 2 six MO's of **1** and five MO's of **2** will be occupied. The occupation of six MO's (anion) will yield only a very small separation between highest occupied (HOMO) and lowest unoccupied MO (LUMO) in case of a large $S_3 - S_7$ separation. This indicates a triplet ground state and thus an unstable structure. A slight distortion towards a shorter $S_3 - S_7$ distance will enlarge the HOMO-LUMO gap[7] and will lead to a net stabilization. This explains the short (2.7 Å) $S_3 - S_7$ distance in **1**. An occupation of only five MO's (cation) yields at short $S_3 - S_7$ distances a small HOMO-LUMO gap but at large $S_3 - S_7$ distances a large one. In addition to this electronic effect comes a smaller nuclear nuclear repulsion term for large $S_3 - S_7$ distances. Both effects will shift the minimum of energy to a structure with large $S_3 - S_7$ distances.

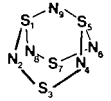
To check these qualitative arguments we have carried out semiempirical calculations using the CNDO/2[8] method. Varying the $S_3 - S_7$ distance and leaving all other distances constant will yield a minimum in the total energy for $S_3 - S_7 = 2.2$ Å for the anion and 4.0 Å for the cation. The calculations confirm the qualitative arguments given above and the sequence of the allylic orbitals presented in Figure 2.

The CNDO/2 and EH results on **1** and **2** provide us with net charges, bond indices[9] and reduced overlap populations[10]. In Table 1 these results for **1** and **2** are listed. As anticipated from a simple consideration of electronegativities we obtain a partial negative charge on the nitrogen centers and a partial positive one on the sulfur atoms. Of special interest in view of recent speculations of making "electron pairs of higher energy"[11] responsible[2,3] for the short S – S distances in **1** and **3** we find for the reduced overlap populations and the bond indices only small values between the nonbonded sulfurs. This indicates no bonding between S_1/S_3, S_3/S_5, S_1/S_7 and S_5/S_7. The results of an energy partitioning for **1** and **2** given in Table 2 lead to the same result.

Related to **1** is the tetrasulfurpentanitridoxide anion **5**[12]. It can formally be derived from **1** by oxidizing one bridgehead sulfur atom. Since the electronic π-system of **1** and **4** respectively is still intact our qualitative model is in accord with the short (2.63 Å for **5**) $S_3 - S_7$ distance. The average SN bond distance (1.62 Å for **5**) is close to that found for **1**.

To derive qualitatively the π molecular orbitals of **3** we proceed analogously to the derivation of structures of **1** and **2**. Instead of replacing X by N which provides one 2p orbital we replace it by a NSN unit which provides formally four π-electrons. The interaction between the π-MO's of this unit with our two allyl fragments of model **4** is predicted to be small. This can be seen by comparing the MO diagram at the left of Figure 2 and that at the left of Figure 3. The latter is the outcome of an EH[6]

Table 1. Bond indices, Mulliken overlap population and net charges for **1** and **2** as derived from an CNDO/2 and EH calculation. In case of the EH method the calculation has been carried out without (sp) and with (spd) 3d orbitals on sulfur



	Bond indices (CNDO/2)						Net charges (CNDO/2)			
	S_1N_2	N_2S_3	S_1S_5	S_1S_3	S_3S_7	S_1N_9	S_1	N_2	S_3	N_9
cation	1.002	1.139	0.015	0.022	0.004	0.881	0.53	−0.18	0.49	−0.29
anion	0.878	1.048	0.026	0.048	0.340	0.930	0.31	−0.36	0.10	−0.39
	Reduced overlap population (EH)						Net charges (EH)			
	S_1N_2	N_2S_3	S_1S_5	S_1S_3	S_3S_7	S_1N_9	S_1	N_2	S_3	N_9
cation (sp)	0.760	0.644	−0.010	−0.071	0.016	0.659	2.18	−1.00	0.94	−1.24
cation (spd)	0.943	0.844	−0.079	−0.072	0.005	0.915	1.28	−0.69	1.09	−0.97
anion (sp)	0.665	0.708	−0.110	−0.124	0.278	0.654	1.65	−1.30	1.17	−1.43
anion (spd)	0.918	0.940	−0.094	−0.099	0.260	0.911	1.10	−0.94	0.82	−1.08

Table 2. Energy partitioning for **1** and **2** as derived from a CNDO/2 calculation (without 3d orbitals). All values in eV

	S_1N_2	N_2S_3	S_1S_5	S_3S_7	S_1N_9	S_1S_3
cation	−15.34	−15.54	1.205	0.865	−13.87	1.233
anion	−13.74	−15.31	0.451	−3.26	−14.33	0.222

calculation using structure **3**. It can be constructed from that of **4** with a short $S_3 - S_7$ distance by adding the three allylic π $1b_2$, $2a_2$ and $3b_2$ of the NSN bridge.

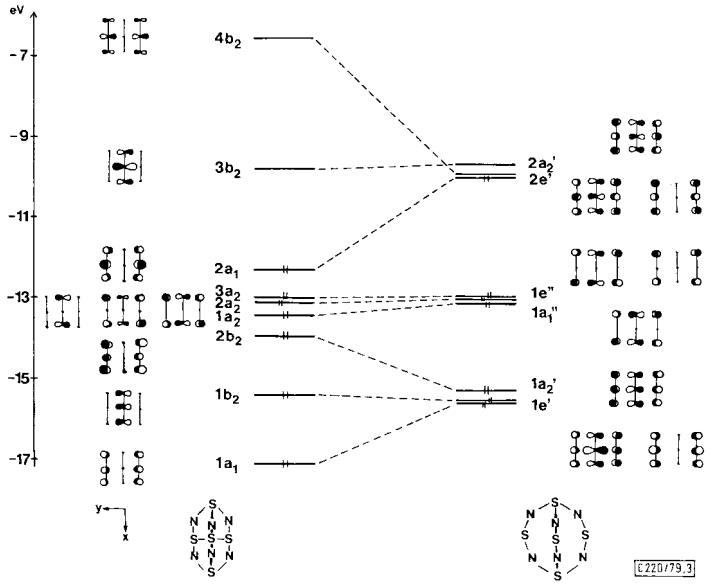
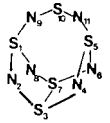


Fig. 3. π-Molecular orbital energies of **3** (C_{2v}) left and **6** (D_{3h})

In Table 3 the Mulliken overlap populations and net charges for **3** are listed.

Table 3. Mulliken overlap population and net charges for **3** as derived from an EH calculation without (sp) and with (spd) inclusion of 3d orbitals on sulfur

	Reduced overlap population							
	S_1N_2	N_2S_3	S_1N_9	N_9S_{10}	S_3S_7	S_1S_5	S_1S_3	S_1S_{10}
(sp)	0.681	0.705	0.607	0.902	0.446	0.001	−0.122	−0.084
(spd)	0.967	1.004	0.822	1.254	0.522	−0.002	−0.121	−0.090

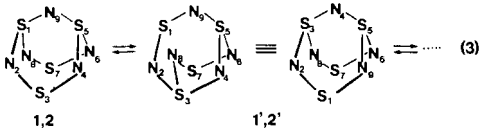


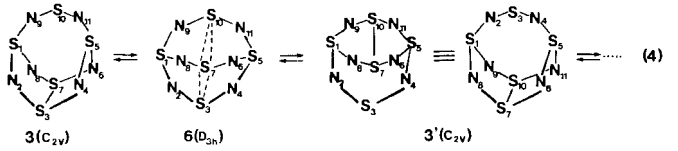
	Net charges				
	S_1	N_2	S_3	N_9	S_{10}
(sp)	1.61	−1.32	1.27	−0.94	1.40
(spd)	1.077	−0.900	0.85	−0.60	0.93

Valence Isomerization of 1 to 3

In case of the bicyclic cage compounds **1** to **3** several intramolecular degenerate rearrangements seem possible as indicated below. The corresponding reaction graphs have been given by *Balaban* [13]. For **1** the rearrangement (3) involves the breaking of the $S_3 - S_7$ bond together with an SN bond shift. For **2** only the NS bond has to be shifted.

In case of the intramolecular rearrangement given in (4) one could envisage a transition state with D_{3h} symmetry. Here the breaking of the S_3-S_7 bond may in part be compensated by interacting with the allylic π-system formed by the $N_9-S_{10}-N_{11}$ bridge.





To explore this possibility we have correlated the π-molecular orbitals of **3** (C_{2v} symmetry) with those of S_5N_6 with D_{3h} symmetry (**6**) in Figure 3.

It is seen from this presentation that for reasons of symmetry the breaking of the S_3-S_7 σ bond in **3** to yield **6** can not be compensated for by interacting with an empty π-orbital of the bridging NSN unit. Thus a considerable activation energy is expected for the degenerate rearrangement indicated in (2). Using the EH method[6] as a guide we predict an energy difference between **6** and **3** of 1.3 eV. According to our simple MO diagram we predict for the dication of **3** a structure close to D_{3h} symmetry. If we remove two electrons from **3** (Figure 3, left) we create a species with a small HOMO-LUMO gap which is unstable with respect to the elongation of the S_3-S_7 bond.

Conclusion

To sum up our results, we can predict stable cage structures with short S_3-S_7 distances in case of model **4** if our bridge provides high lying filled b_2 orbitals (e.g. X≡ N^-, O, S, CR_2, C_2H_2, NSN, $C_3H_3^-\cdots$). Structures with long S_3-S_7 bonds are predicted if the bridging atom or group provides low lying empty orbitals (e.g. N^+, CR^+, B-R, $C_3H_3^+$, $NSN^{++}\cdots$). As a further application of these rules we consider the structures of β-P_4S_5[14] and As_4S_5[15]. To understand both structures we start with M_4S_4 (M = P, As) which can be rationalized using a simple MO model[4]. Bridging the M_1-M_5 centers by an electron rich bridge (S, M^-) leads to a cage structure with a short M_3-M_7 distance as found experimentally (see (2)). A bridge with an electron acceptor (M^+, S^{++}) should lead to structures with large M_3-M_7 distances.

Calculations

The parameters for the extended Hückel calculations were those reported in ref.[4] and [5]. For model **4** we assumed the same structural parameters as for **3**[3]. The NSN bridge was replaced by two H atoms. For **6** the NS bond length between the bridgehead sulfur atoms and the adjacent nitrogen centers were assumed to be 1.7 Å, all other

N–S bond lengths were taken 1.54 Å. For all other structures the experimental geometries were used.

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