The Structures of $S_4N^\ominus$, $S_3N_2O_2$ and $S_4N_3^\ominus$

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Dedicated to Professor Josef Goubeau on the occasion of his 80th birthday

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Structural Isomers, MNDO Calculations, Transannular Interactions

Part of the potential surface of $S_4N^\ominus$ has been investigated using the MNDO method. It is found that the *cis-trans* isomer **1b** is more stable by 20–30 kJ/mol than the *trans-trans* isomer (**1c**) and the *cis-cis* isomer (**1a**). The stability of **1b** is traced back to stabilization of the HOMO and to a Coulomb attraction. For $S_3N_2O_2$ (**2**) the MNDO calculations favour those isomers (**2a** and **2b**) with two sickle-like arrangements for the same reasons. For $S_4N_3^\ominus$ (**3**) only one isomer (**3a**) is favoured due to the stabilization of the HOMO. The similarity in the transannular interaction present in **1–3** and that in trithiapentalenes and related compounds is pointed out. The PE spectrum of **2** has been reinvestigated. The first five bands can be interpreted by comparison between the measured ionization potentials and the calculated (MNDO) orbital energies.

Recently the structures of three sulfur nitrogen compounds have been reported containing at least one sickle-like arrangement: $S_4N^\ominus$ (**1**) [1], $S_3N_2O_2$ (**2**) [2] and $S_4N_3^\ominus$ (**3**) complexed to Pt [3]. Structural data for all three compounds are displayed in Fig. 1. Common to all three structures are transannular S...S, S...O and S...N distances below the sum of the corresponding van der Waals radii.

Fig. 1. Bond lengths of $S_4N^\ominus$, $S_3N_2O_2$ and S_4N_3PtCl .

To explain the structure of $S_4N^\ominus$ *ab initio* calculations using Slater type basis functions have been carried out [1]. These investigations indicate an 8π system with relatively strong negative charges (–.42, –.44) at the terminal sulfur centers and the nitrogen (–0.35). The configuration found for **1** is tentatively ascribed as due to an electrostatic interaction between terminal and internal sulfur atoms. For the latter positive charges (0.01 and 0.20) are predicted.

In connection with our interest in possible isomerizations latent in compounds containing sulfur and nitrogen [4] the most likely configurations of **1–3** were of interest.

Specific questions are:

1. What is the energy difference between different isomers?
2. Why are the configurations found in Nature preferred? and in case of **1** (where the relatively small number of atoms allows the calculation of a surface):
3. What are the transition states between the different configurations?

To answer these questions we have carried out molecular orbital (MO) calculations using the MNDO model [5].

Calculations on $S_4N^\ominus$ (**1**)

In case of $S_4N^\ominus$ we have investigated the potential energy as a function of the angles α and β (in plane movement) by varying them from 105 to 270° independently, starting from the *cis-cis* conformation (**1a**) shown below. A second potential surface has been derived by changing the angles γ and δ (out of plane movement) independently. One parameter (γ) was varied from 0° to 360°, the other one (δ) from 0 to 180°. All other geometrical parameters were optimized with respect to the energy. The potential surfaces obtained for the two pairs of variables (α, β on one side and γ, δ on the other) look very similar in so far as both exhibit equivalent

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Fig. 2. Total energy of $S_4N^\ominus$ as a function of γ and δ . The contours are drawn for every 0.1 eV. For the meaning of T_1 , T_2 , P_1 and P_2 see text. Around P_1 and P_2 self consistency could not always be achieved therefore the energy contours could not be drawn.

minima for the *cis-trans* isomers **1b** and **1b'** and local minima for the *cis-cis* isomer (**1a**) and the *trans-trans* isomer (**1c**). As an example we show the energy map resulting from the out-of-plane movement of the terminal S atoms in Fig. 2. It turned out that the in plane movement of the terminal S atoms affords more energy than the changes of γ and δ . The potential surface in Fig. 2 shows three minima for $\delta = 180^\circ$, $\gamma = 0^\circ$ (**1b**), $\delta = 0^\circ$, $\gamma = 180^\circ$ (**1b'**) and $\gamma = 360^\circ$, $\delta = 180^\circ$ (**1b'**). Local minima are encountered for $\gamma = 0^\circ$, $\delta = 0^\circ$ (**1a**), $\gamma = 360^\circ$, $\delta = 0^\circ$ (**1a**) and $\delta = 180^\circ$, $\gamma = 180^\circ$ (**1c**). The heat of formations of **1a**, **1b** and **1c** are given in Tab. I. Further distinguished points of the potential surface are two peaks, P_1 and P_2 , for turning S^4 and S^5 out of the molecular plane defined by $S^2N^1S^3$. One peak, P_1 ,

corresponds to the conformation where S^4 and S^5 are syn to each other the other one, P_2 , where S^4 and S^5 are anti to each other. The path of minimum energy from **1b** ($\delta = 180^\circ$, $\gamma = 0^\circ$) to **1b'** ($\delta = 0^\circ$ or 360° , $\gamma = 180^\circ$) via the *trans-trans* isomer **1c** is predicted to be only slightly lower than via **1a**. The geometry of the corresponding transition states (T_1 , T_2) (all remaining geometrical parameters optimized is given in Table I).

In Fig. 3 the energy profiles along the two different paths, **1b**- T_1 -**1c** and **1b**- T_2 -**1a** are depicted.

Fig. 3. Energy profiles along the paths **1b**- T_1 -**1c** and **1b**- T_2 -**1a** of Fig. 2.

Table I. Calculated geometrical parameters for different configurations of **1** according to the MNDO model.

Configuration	Bond lengths [Å]				Bond angles [°]					H_f [kJ/mol]
	N^1S^2	N^1S^3	S^2S^4	S^3S^5	$S^2N^1S^3$	$N^1S^2S^4$	$N^1S^3S^5$			
1a	1.546	1.546	1.852	1.852	144	120	120	0	0	73.66
1b	1.562	1.558	1.863	1.864	127	106	113	180	0	42.30
1c	1.573	1.573	1.863	1.863	117	108	108	180	180	61.28
T_1	1.536	1.644	1.846	1.880	116	109	105	90	180	119.66
T_2	1.518	1.625	1.837	1.888	131	105	119	90	0	122.24

Table II. Calculated Wiberg bond indices and net charges of **1** according to the MNDO model.

Configuration	N ¹ -S ²	N ¹ -S ³	S ² -S ⁴	S ³ -S ⁵	S ⁴ -S ⁵	S ² -S ⁵	N ¹	S ²	S ³	S ⁴	S ⁵
1a	1.28	1.28	1.06	1.06	0.024	—	-.40	.34	.34	-.64	-.64
1b	1.33	1.30	1.06	1.04	—	0.067	-.34	.36	.31	-.64	-.68
1c	1.31	1.31	1.04	1.04	—	—	-.28	.25	.25	-.61	-.61

The energy difference between the minima is relatively small (20–30 kJ/mol). It is interesting to notice that the sickle-like structure, **1b**, is favoured by about 20–30 kJ/mol as compared with other isomers. A second result worth to keep in mind is the relatively low energy barrier (50–80 kJ/mol) between the different valleys. The prediction that the change of γ and δ (out of plane movement) is more economical for $S_4N^\ominus$ than the change of α and β (in plane movement) in any case can be traced back to the fact that we are dealing with an 8π system, *i. e.* four of the five π -niveaus are occupied and thus the π -bond order is reduced because one π^* orbital is occupied as well. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of **1** in **1b** are shown schematically below. From this

drawing it is evident that in case of the *cis-trans* isomer (**1b**) the spatial interaction between S² and S⁵ contributes to the lowering of its energy. This analysis is in line with a treatment dealing with the stability of isomers of extended π systems given by Hoffmann and Olofson [6]. The overlap populations

and atomic charges predicted according to the MNDO model are given in Table II. Both results parallel those obtained by *ab initio* methods [1].

Calculations on $S_3N_2O_2$ (**2**) and $S_4N_3^\ominus$ (**3**)

Due to the larger number of atoms of $S_3N_2O_2$ (**2**) compared with $S_4N^\ominus$ more configurations are possible in a chain-arrangement. The most likely ones

are **2a–2e** for which a planar arrangement with a bent NSO group is pertained. Using again the MNDO method [5] we have calculated their structures by minimizing the energy with respect to all geometrical parameters. The resulting structural parameters as well as the heat of formation (H_f) are given in Table III. According to these results those structures with two sickle-like arrangements (**2a** and **2b**) are more stable than the structures with

Table III. Calculated geometrical parameters and heat of formation (H_f) for different configurations of **2** according to the MNDO method.

Con- figu- ra- tion	Bond lengths [Å]						Bond angle [°]					H_f [kJ/mol]
	S ¹ -N ²	N ² -S ⁴	S ⁴ -O ⁶	S ¹ -N ³	N ³ -S ⁵	S ⁵ -O ⁷	N ² -S ¹ -N ³	S ¹ -N ² -S ⁴	N ² -S ⁴ -O ⁶	S ¹ -N ³ -S ⁵	N ³ -S ⁵ -O ⁷	
2a	1.610	1.526	1.482	1.610	1.526	1.482	96	129	111	129	111	523.91
2b	1.584	1.522	1.478	1.602	1.523	1.481	97	142	113	132	110	518.60
2c	1.623	1.550	1.482	1.623	1.550	1.482	96	117	104	117	104	577.88
2d	1.611	1.528	1.482	1.621	1.547	1.482	96	128	111	119	104	549.98
2e	1.585	1.523	1.475	1.612	1.543	1.481	97	141	114	121	105	549.61

Table IV. Calculated Wiberg bond indices and net charges of **2** according to the MNDO method. For the numbering of the atoms see text.

Confi- guration	Wiberg bond indices								Net charges						
	S1-N ²	S1-N ³	N ² -S ⁴	N ³ -S ⁵	S ⁴ -O ⁶	S ⁵ -O ⁷	S1-O ⁶	S1-O ⁷	S ¹	N ²	N ³	S ⁴	S ⁵	O ⁶	O ⁷
2a	1.039	1.039	1.488	1.488	1.338	1.378	0.053	0.053	.40	-.50	-.50	.87	.87	-.57	-.57
2b	1.068	1.017	1.447	1.472	1.355	1.338	0.056	0.053	.47	-.55	-.57	.89	.90	-.56	-.58
2c	1.038	1.038	1.471	1.471	1.382	1.382	0.049	0.049	.22	-.42	-.42	.78	.78	-.47	-.47
2d	1.042	1.037	1.496	1.468	1.335	1.381	0.053	0.049	.32	-.47	-.45	.87	.80	-.57	-.48
2e	1.065	1.018	1.440	1.446	1.376	1.382	0.058	0.051	.39	-.54	-.53	.89	.81	-.53	-.48

one sickle-like arrangement (**2d** and **2e**). The structure **2c** with the all trans arrangement is even less stable than **2d** and **2e**. The energy difference between **2c** and **2d** and **2e** is 28 kJ/mol. The difference between the latter and **2a** and **2b** amounts to 26 and 31 kJ/mol respectively. Both differences suggest that the gain due to transannular interactions for one sickle-part is in the order of 26–30 kJ/mol. A similar energy difference is predicted between the H_f -values for **1b** compared with **1a** and **1c**. Analogous to **1** stabilization of **2a** and **2b** can be traced back to a Coulomb interaction between the negatively charged oxygen centers and the positively charged sulfur atoms and to an in-phase relation of the HOMO in a sickle arrangement. The HOMO and

relation leads to a weakly bonding interaction as can be seen from the Wiberg bond indices [7] given in Table IV. Parallel to this interaction there is a strong Coulomb attraction between the central S atom and the oxygen atoms as seen from the calculated net charges (Table IV).

Related to the structure of **2** is $S_4N_3^{\ominus}$ (**3**) in so far as five of the seven π -orbitals are occupied. It has been isolated recently as a ligand in the S_4N_3 PtCl complex [3]. As in the case of **2** five configurations (**3a–3e**) seem most likely. The heats of formation

LUMO of **2** in **2a** as derived by an MNDO calculation is sketched below. It is seen that in this sickle-like arrangement the coefficient of the O atomic orbital (p_zAO) in the HOMO has the same sign as the AO coefficient at the sulfur atoms. This in-phase

calculated for **3a–3e** are listed in Table V together with the bond lengths and angles. It is seen that configuration **3a** is predicted to be the most stable one, but the difference in the heat of formation to **3d**, **3b** and **3c** is relatively small and within the

Table V. Calculated geometrical parameters, heat of formation (H_f) and net charges for different configuration of **3** according to MNDO. For the numbering see formulas in the text.

Con- figu- ra- tion	Bond length [Å]							Bond angles [°]							Net charges							H_f kJ/mol
	N ¹ -S ²	N ¹ -S ³	S ² -N ⁴	S ³ -N ⁵	N ⁴ -S ⁶	N ⁵ -S ⁷		S ² -N ¹ -S ³	N ¹ -S ² -N ⁴	N ¹ -S ³ -N ⁵	S ² -N ⁴ -S ⁶	S ³ -N ⁵ -S ⁷			N ¹	S ²	S ³	N ⁴	N ⁵	S ⁶	S ⁷	
3a	1.633	1.633	1.579	1.579	1.513	1.513		108	109	109	129	129			-.615	.191	.191	-.181	-.181	-.202	-.202	336.77
3b	1.606	1.622	1.569	1.578	1.522	1.515		122	122	107	128	129			-.657	.314	.273	-.235	-.190	-.283	-.221	344.34
3c	1.643	1.643	1.594	1.594	1.523	1.523		106	101	101	117	117			-.550	.163	.163	-.107	-.107	-.281	-.281	345.99
3d	1.637	1.639	1.579	1.594	1.513	1.524		107	108	101	129	117			-.583	.183	.174	-.176	-.105	-.203	-.288	341.16
3e	1.610	1.629	1.569	1.595	1.521	1.523		120	123	100	128	117			-.620	.297	.242	-.229	-.130	-.274	-.278	352.23

error limit of the method. It is interesting to notice that for **3** the calculation predicts partial negative charges for the terminal sulfur atoms (S^6 and S^7) as well as for the central nitrogen atom (N^1) (see Table V). The Coulomb attraction argument for the preference of **3a** fails in this case. As anticipated the HOMO and LUMO for **3** show the same nodal properties as in case of **2** and thus because of the relative short N^1S^6 and N^1S^7 distance the stability of **3a** can be understood in terms of transannular bonding interactions in the HOMO.

PE Spectrum of **2**

A further check for the validity of the MNDO results is provided by comparison of the ϵ_j values with the vertical ionization potentials, $I_{v,j}$, derived from the He(I) photoelectron (PE) spectrum of **2**. Since our assignment differs from that reported in the literature (see Table VI) [8] with respect to the number of bands for the broad peak around 11.2 eV, we have remeasured the PE spectrum (see Fig. 4). We find three peaks below 13 eV; two of them (bands **1** and **5**) are well separated from a third broad one consisting of three strongly overlapping bands (bands **2–4**). A comparison with the orbital energies, ϵ_j , calculated by MNDO shows an excellent agreement if we assume the validity of Koopmans' theorem ($-\epsilon_j = I_{v,j}$) [9].

Table VI. Comparison between measured vertical ionization potentials, $I_{v,j}$, and calculated (MNDO) orbital energies, ϵ_j , of **2a** (C_{2v}) and **2b** (C_s). All values in eV.

Bands	$I_{v,j}$	ϵ_j (2a)*	ϵ_j (2b)*
1	9.25	— 9.55 ($3b_1, \pi$)	— 9.34 ($5a'', \pi$)
2	11.08	— 11.23 ($2a_2, \pi$)	— 11.19 ($4a'', \pi$)
3	11.38	— 11.51 ($8a_1, n$)	— 11.39 ($15a', n$)
4	11.60	— 11.64 ($7b_2, n$)	— 11.58 ($14a', n$)
5	12.51	— 12.35 ($7a_1, n$)	— 12.68 ($13a', n$)

* The numbering refers to the valence orbitals only.

Final Remarks

The stability of those isomers with transannular interactions resulting in relatively short $S \cdots S$ (**1b**) and $S \cdots O$ (**2a**) distances below the sum of the van der Waals radii resembles very much the situation in trithiapentalenes and related species [10]. In these compounds the preponderance of the U shape has been ascribed to a "delicate balance between the repulsive interactions (repulsion of the nuclei and the lone pairs) and attractive forces ($p\pi$ - $p\pi$ interaction and p_σ -3d or 4s interaction)" [10]. In this connection it is interesting to notice that we have not included 3d or 4s orbitals on the sulfur

Fig. 4. He(I) photoelectron spectrum of **2**.

centers in our basis set and yet our model calculations reproduce experimental results for **1** and **2** remarkable well. This good agreement suggests that also our results concerning the stability of **2b** are reliable and its existence should at least be detectable in the gas phase or in solution. The fact that **2a** only has been isolated in the solid state might be

due to packing effects. In view of the relatively small energy differences between **1b** and **1a** it might be worthwhile to offer $S_4N^{\ominus}$ different cations.

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