sesquioxides, we are focusing our attention on measurement of enthalpies of formation of Am_2O_3 and Cf_2O_3 in order to establish the thermochemical regularities of this important set of compounds in relation to the aqueous ions.

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Structure of Tetrasulfur Dinitride

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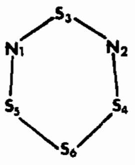
The structure of the six-membered ring S_4N_2, which was predicted to be planar by a CNDO/2 calculation, has been investigated by use of extended Hückel calculations. Our results show that the molecule should have the half-chair conformation, which is in good agreement with an X-ray crystallographic analysis. The results have been rationalized within an MO framework. The structures of related six-membered rings $S_4N_2^{2+}$, $S_4N_2^{2-}$, $S_3N_3^-$, $S_3N_3^+$, S_6, and S_6^{2+} are discussed briefly.

Introduction

The structures of a large number of compounds containing rings or chains of alternating sulfur and nitrogen only have been reported.[1,2] This class of compounds has frustrated chemists for a long time because various structure determinations have often shown that structures which had been predicted for these compounds were wrong.[3] One of the examples is tetrasulfur dinitride.

The structure of the molecule S_4N_2 has been the subject of several studies.[3-5] Nelson and Heal[4] reduced the number of structural alternatives to structure **1** by use of mass, vibrational, and ^{14}N NMR spectroscopy and dipole moment measurements. But they could not make a firm assignment regarding the conformation. Jolly[3] suggested a half-chair conformation in which the sulfur atom S_6 in structure **1** was tilted out of the plane of the other five atoms. However, in 1978, Adkins and Turner predicted a planar conformation on the basis of CNDO/2 calculations. Recently a low-temperature X-ray crystallographic analysis by Chivers[6] showed that the six-membered ring S_4N_2 has the half-chair conformation illustrated in Figure 1. Small, Banister, and Hauptman[7] report a similar result from their X-ray structure determination.



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In this paper we have carried out extended Hückel calculations[8] for S_4N_2 in an attempt to understand conformational preferences of six-membered rings. Although the method can be expected to be quantitatively poor, it seems to be qualitatively correct[9] and it captures the essence of energy changes that accompany variations of bond angles.[10] Surprisingly, our results for S_4N_2 are quantitatively in good agreement with the X-ray experiments.[6,7] A comparison with CNDO/2 calculations[5] has been made, and the results have been rationalized within an MO framework. Extended Hückel calculations on $S_3N_3^-$ and S_6 were also performed, and the structures of related six-membered rings $S_4N_2^{2+}$, $S_4N_2^{2-}$, $S_3N_3^-$, $S_3N_3^+$, S_6, and S_6^{2+} are discussed briefly. This work is part of a larger study of the electronic structures of inorganic rings.[2]

Details of the Calculations

In all of the calculations presented here, we used the computer program ICON8.[11] The following set of Coulomb integrals and orbital exponents is built into the program: $H_{ii}(2s) = -26.0$ eV, $H_{ii}(2p) = -13.4$ eV, $\zeta(2s) = \zeta(2p) = 1.95$ for nitrogen; $H_{ii}(3s) = -20.0$ eV, $H_{ii}(3p) = -13.3$ eV, $\zeta(3s) = \zeta(3p) = 1.817$ for sulfur. We also used the charge iteration feature of the program with the following iteration parameters: $B = 13.7$, $C(2s) = 26.4$, $C(2p) = 13.4$ for nitrogen; $B = 9.70$, $C(3s) = 22.50$, $C(3p) = 11.94$ for sulfur. We did not include a 3d basis function for sulfur because to do so would have greatly increased the computer requirements, and the work of others[10,12] indicates that sulfur 3d AO's can be safely neglected in work on similar problems.

The geometric parameters of S_4N_2 were taken from the X-ray results (see Figure 1). For the geometry of $S_3N_3^-$ we assumed a hexagon with the S–N bond length of 1.60 Å and the bond angles $\angle S = 117°$, $\angle N = 123°$; the structure was based on X-ray experimental data.[13] The structure of S_6 has been determined by two different groups,[14,15] and we used the bond length 2.068 Å from the more recent work.[15]

Results and Discussions

S_4N_2. According to Jolly's suggestion[3] and Nelson and Heal's experiments,[4] the possible conformations of S_4N_2 are planar, boat, chair, and half-chair. We define the angle be-

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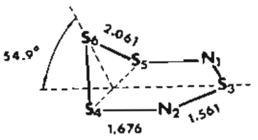

Figure 1. Half-chair structure of S_4N_2. Bond angles are 122.9° at S_3, 126.7° at N, 102.9° at S_6, and 103.4° at S_4.

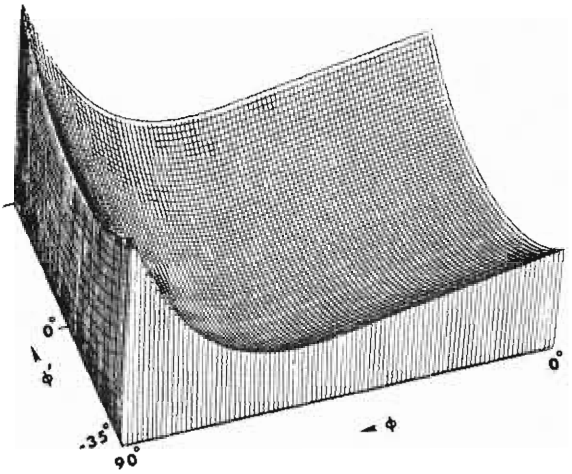

Figure 2. EHMO total energy plots for the ground state of S_4N_2 with various values of ϕ and ϕ'.

tween planes $S_4S_5S_6$ and $N_1N_2S_4S_5$ as ϕ and the angle between planes $N_1S_3N_2$ and $N_1N_2S_4S_5$ as ϕ' (see Figure 1). Extended Hückel calculations of the system with various values of ϕ and ϕ' were performed. The total energy E of the system is a function of angles ϕ and ϕ', and the resultant potential surface $E(\phi,\phi')$ is plotted in Figure 2. The area $\phi > 0°$, $\phi' > 0°$ represents the boat conformation, the area $\phi > 0°$, $\phi' < 0°$ represents the chair conformation, and the axes $\phi = 0°$ and $\phi' = 0°$, are the half-chair. Figure 2 exhibits a minimum total energy at $\phi' = 0°$, $\phi = 55°$, which is in remarkable agreement with the X-ray analysis[6] (see Figure 1, $\phi = 54.9°$). The calculated total energy for the planar geometry is 0.6 eV higher than that for the half-chair with $\phi = 55°$. In marked contrast to our result, Adkins and Turner[5] found the calculated total energy for the planar structure to be 0.7 eV lower than that of the half-chair with $\phi = 45°$ so that they concluded that the planar conformation is most stable. However, their geometric parameters were different from ours, and we felt it was worth repeating the extended Hückel calculations with their parameters. The results still show that the half-chair conformation is favored over the plane, but the optimum value of the angle ϕ turns out to be about 50°. Furthermore, we found that the relative stabilities of ring conformations do not seem to be affected by small changes in the values of Coulomb integrals and charge iteration parameters. We have carried out the calculations without the charge iteration procedure, and the results are qualitatively the same as those above.

The conformational results may be rationalized by comparison of the reduced overlap populations[16] for the different structures. The values of the populations are plotted in Figure 3. It is clear that the effects of flipping atom S_6 out of the plane are primarily the following: (i) increase of bonding character between neighboring sulfur atoms and between S_3 and its neighboring nitrogen atoms and (ii) increase of antibonding character between S_6 and the transannular nitrogen atoms and sulfur S_3. Since the increment of the bonding overlap population is larger than that of the antibonding, the total energy of the system is lowered by moving the atom S_6 out of the plane to $\phi = 55°$. With angle ϕ increasing from 55 to 90° the antibonding character of S_6–N and S_6–S_3 increases much more quickly than the bonding characters of S_6–S_4, S_6–S_5, and S_3–N. Therefore, the total energy of the system rises from $\phi = 55°$ to $\phi = 90°$. This is not surprising since the distances S_6–N and S_6–S_3 shorten more quickly in going from $\phi = 55°$ to $\phi = 90°$ than in going from $\phi = 0°$ to $\phi = 55°$. The values of distances are listed in Table I. On the other hand, as the atom S_3 is flipped out of the plane, the transannular antibonding interaction between S_3 and other sulfur atoms is increased and the bonding interaction between S_3 and neighboring nitrogen atoms is decreased. Thus the total energy of the system increases from $\phi' = 0°$ to $\phi' = 45°$.

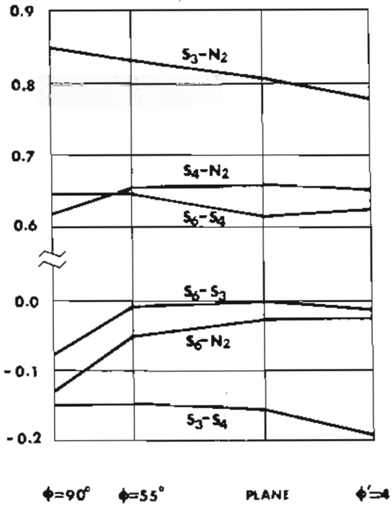

Figure 3. Overlap population plots for various conformations of S_4N_2.

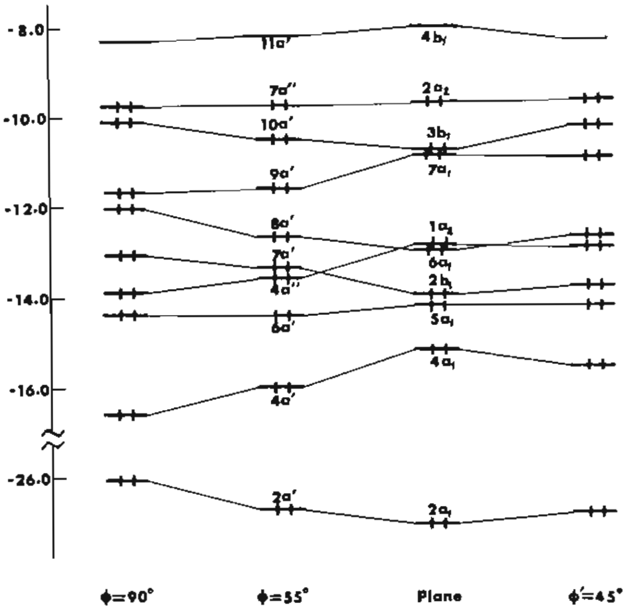

Figure 4. Correlation of some EHMO energy levels between different conformations of S_4N_2.

Table I. Distances (Å) of S_6–N and S_6–S_3 for Different Values of ϕ

	$\phi = 0°$	$\phi = 55°$	$\phi = 90°$
S_6–N	2.79	2.44	1.88
S_6–S_3	3.69	3.31	2.73

In order to make the above explanation clearer, Figure 4 correlates some of our extended Hückel energy levels for different conformations. The orbitals omitted in Figure 4 change little in energy. The molecular orbitals that are pri-

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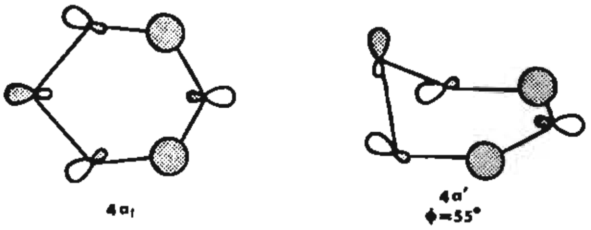
(16) J. P. Lowe, "Quantum Chemistry", Academic Press, New York, 1978, p 297.

marily responsible for the energy changes are shown in **2**–**8**.

There are three orbitals $4a_1$, $7a_1$, and $1a_2$ that are mainly responsible for the energy decrease in going from $\phi = 0°$ to $\phi = 55°$. For the planar geometry, $4a_1$ and $7a_1$ are σ orbitals and $1a_2$ is a π orbital (see **2**–**4**). The bonding interaction between S_6 and neighboring sulfur atoms in orbital $4a_1$ is increased in going from $\phi = 0°$ to $\phi = 55°$ due to the increasing in-phase overlap between p_z orbitals of S_6 and its neighbors. In the orbital $7a_1$, the interactions between S_3 and the nitrogen atoms are antibonding and the out-of-phase overlap decreases in flipping the atom S_6 out of the plane. $1a_2$ is a typical π orbital with bonding interactions between $S_4S_5S_6$ and $N_1S_3N_2$ units, which were not found in Adkins and Turner's calculations.[5] Flipping the $S_4S_5S_6$ unit from $\phi = 0°$ to $\phi = 55°$ raises the bonding overlap of S_6–S_4 and S_3–N from 0 to 0.017 and 0.014, respectively.



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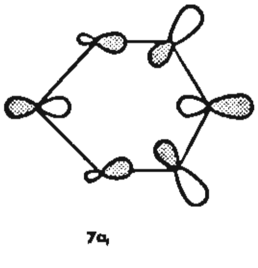

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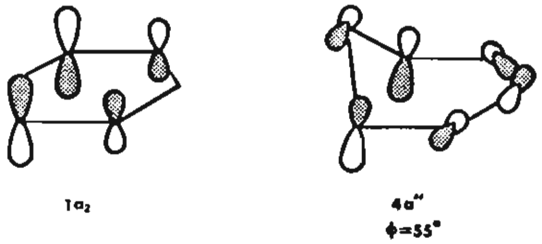

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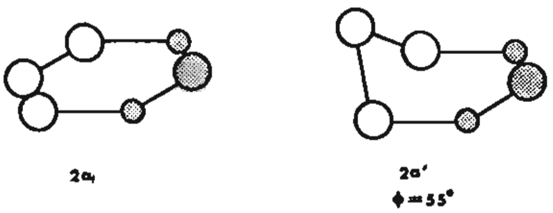
The energies of orbitals $2a_1$, $2b_1$, $6a_1$, and $3b_1$ increase when the atom S_6 is tilted out of the plane. $2a_1$ largely consists of s valence orbitals of the six atoms, and the interaction between units $S_4S_5S_6$ and $N_1S_3N_2$ is antibonding (see **5**). The out-of-phase overlap populations of S_6–N and S_6–S_3 increase by −0.004 and −0.008, respectively, when the angle ϕ is increased to 55°. In going further to $\phi = 90°$, the antibonding overlap populations are raised dramatically (by −0.015 and −0.044, respectively). $2b_1$ is a π orbital with bonding character among S_4, S_5, and S_6 and among N_1, S_3, and N_2 and with antibonding character between S_4 and N_2 and between S_5 and N_1 (see **6**). $6a_1$ is a σ orbital with the same bonding and antibonding character as $2b_1$ (see **7**). When the atom S_6 or S_3 is flipped out of the plane, the bonding overlap drops; however, the antibonding overlap remains nearly constant. Thus the two energy levels go up. $3b_1$ is a π orbital that is antibonding between S_6 and N, between S_3 and S_4, and between S_3 and S_5 (see **8**). The out-of-phase overlap population between S_6 and N is raised from near 0 to −0.015 and −0.036 in going from $\phi = 0°$ to $\phi = 55°$ and 90°, respectively. On the other hand, if we lift the atom S_3 out of the plane to $\phi' = 45°$ (see **8**), the antibonding overlap between S_3 and S_4 or S_5 rises by −0.022. It seems that $3b_1$ is the main orbital responsible for raising the total energy of the system in going from plane to half-chair with $\phi' = 45°$.



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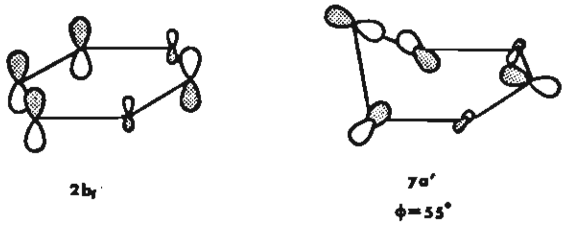

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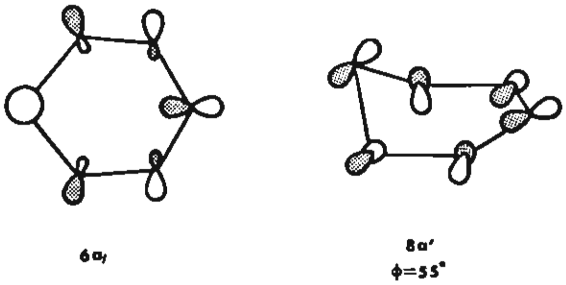

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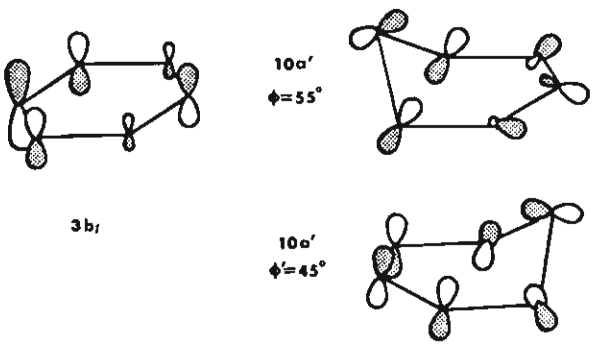

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It turns out that the strong stabilization of $4a_1$, $7a_1$, and $1a_2$ outweighs the destabilization of $2a_1$, $2b_1$, $6a_1$, and $3b_1$ in raising the atom S_6 out of the plane to $\phi = 55°$. However, the stabilization is overruled by the destabilization in going further to $\phi = 90°$ or in moving the sulfur atom S_3 out of the plane.

It is of interest to note that the energy of the HOMO $2a_2$ for S_4N_2 has been lowered little by changing the angles ϕ and ϕ', and the LUMO $4b_1$ dropped somewhat but the energy changes of the LUMO $4b_1$ for different ϕ and ϕ' are much smaller than the total energy differences between the corresponding conformations (see Figure 4). It seems that the anion $S_4N_2^{2-}$ and cation $S_4N_2^{2+}$ would still prefer half-chair structures, should they exist. However, Bhattacheryya et al.[17] assumed that these ions have planar geometries.

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[17] A. A. Bhattacharyya, A. Bhattacheryya, R. R. Adkins, and A. G. Turner, *J. Am. Chem. Soc.*, **103**, 7458 (1981).

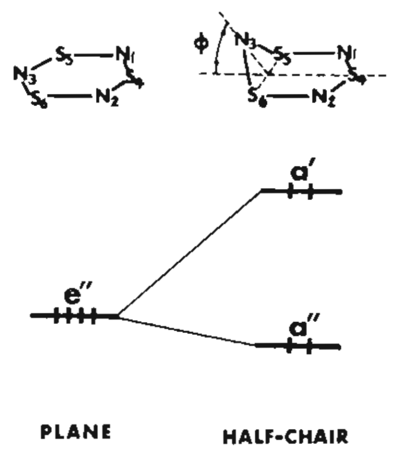
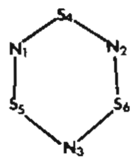


Figure 5. HOMO of $S_3N_3^-$ split into two single orbitals in going from the plane to the half-chair.

$S_3N_3^-$. $S_3N_3^-$ and S_4N_2 are isoelectronic. Both of them have 34 valence electrons, and if planar geometries are assumed, both would have 10 π electrons. Recently the synthesis, X-ray structure determination, and theoretical studies of $S_3N_3^-$ have been done by several workers.[13,17-22] They concluded that the six-membered ring $S_3N_3^-$ preferred a planar D_{3h} geometry (see **9**), although in the particular case of the cesium salt it was puckered.[19] We have carried out extended Hückel calculations of the planar structure with bond lengths S–N = 1.60 Å and angles ∠S = 117°, ∠N = 123° and also several chair, boat, and half-chair conformations by moving atom S_4 or N_3 out of the plane and keeping the lengths S–N = 1.60 Å and angles $\angle S_4 = 117°$, $\angle N_3 = 123°$ constant. Our results show that the planar structure is more stable than others. This is in agreement with X-ray results.[13,18,19]



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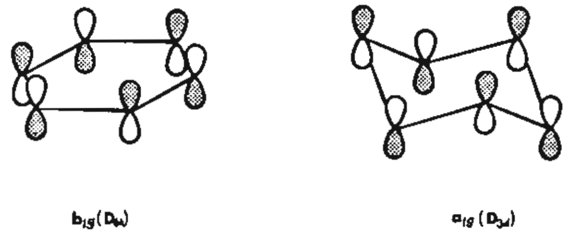
In contrast with S_4N_2, the bonding characters of N_3–S_5, N_3–S_6, S_4–N_1, and S_4–N_2 of $S_3N_3^-$ decrease on flipping atom N_3 out of the plane. Therefore, the half-chair conformation is less stable than the plane.

It is worth noting the HOMO of $S_3N_3^-$, e″, which is a doubly degenerate orbital. If the cation $S_3N_3^+$ maintained planar geometry, it would be a highly reactive species. However, the HOMO e″ splits into two nondegenerate orbitals on going from the plane to the half-chair with atom N_3 being raised out of the plane to an angle ϕ (see Figure 5). And the total energy of the planar structure for $S_3N_3^+$ is 0.24 eV higher than that of the half-chair with $\phi = 80°$. This feature of the electronic structure suggests that the cation $S_3N_3^+$ might prefer the half-chair conformation.

S_6. S_6 has 36 valence electrons, two more than S_4N_2. The six-membered S_6 ring has a chair conformation (D_{3d}) with bond length 2.068 Å and bond angle β = ∠S–S–S = 102.6°.[15] Semiempirical molecular orbital calculations have been carried out by Miller and Cusachs[23] and Meyer et al.[24] to explain the spectrum of S_6. Salahub, Foti, and Smith[25] have used SCF–Xα calculations to study the structures of S_6, S_6^{2+}, and higher charged cations as well as other neutral and cationic S_n clusters. For the six-atom system they included diagrams relating MO energy levels from triangular-prismatic, boat, and chair shapes but not the planar and half-chair forms. We performed extended Hückel calculations for the six-membered ring S_6 with constant bond length 2.068 Å and several values of bond angle β. The calculated total energy of the system exhibits a minimum at $\beta = 107.5°$, agreeing qualitatively with the experimental bond angle. We did not attempt to find parameters that allow the calculations to produce the experimental value of angle β.[25]

In marked contrast with S_4N_2, the energy level of the HOMO of the puckered ring ($\beta = 107.5°$) is 0.9 eV lower than that of the planar ring. A comparison of the HOMO of the planar and puckered rings is shown in **10**. The orbital b_{1g} in the planar ring is a typical antibonding π orbital with equal coefficients of alternant sign on each sulfur atom. Puckering the planar ring produces somewhat σ-type bonding overlap between the 3p AO's on neighboring atoms. Thus the highest occupied energy level drops dramatically. This rationalizes why the six-membered S_6 ring prefers the puckered ring structure and also hints that the cation S_6^{2+}, which, if it exists, would be isoelectronic with S_4N_2 and $S_3N_3^-$, might prefer a planar conformation.



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Conclusion

In contrast with previous CNDO/2 calculations,[5] our extended Hückel results show that a half-chair conformation for the six-membered ring S_4N_2 is favored over other conformations. Moreover, the calculated tilt angle ϕ is in excellent agreement with the X-ray result[6] by use of the charge iteration feature and reasonable Coulomb integrals that were built into the computer program. We were surprised at the quantitative agreement with the experimental data without the need for special parameters. The half-chair conformer is a compromise between the antibonding character of transannular sulfur–nitrogen and sulfur–sulfur atoms and the bonding character of neighboring sulfur–sulfur and sulfur–nitrogen atoms. The rule also applies to ions $S_4N_2^{2+}$, $S_4N_2^{2-}$, and $S_3N_3^+$ if they exist. But the six-membered ring $S_3N_3^-$ and possible cation S_6^{2+}, which are isoelectronic with S_4N_2, prefer a planar geometry. Another related six-membered ring S_6 with the highest symmetry should have a chair conformation. The calculated bond angle β is in qualitative agreement with the X-ray result.

Registry No. S_4N_2, 12033-57-7.

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(26) For example, the calculated value of angle β would be 104° if we take the orbital exponents $\zeta(3s) = \zeta(3p) = 1.967$ instead of 1.817.