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The Structure of the Cyclopentathiazenium Cation ($S_5N_5^+$)[1]

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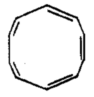
A parallelism between the structural problems present in [10]annulene and the 14π system of $S_5N_5^+$ is pointed out. Comparison of six possible structural isomers of $S_5N_5^+$ within an MO framework leads to the conclusion that an azulene-like structure of $S_5N_5^+$ is preferred. The electronic spectrum of $S_5N_5^+$ is discussed briefly.

Introduction

Recently two research groups reported different structures for the cyclopentathiazenium ($S_5N_5^+$) cation: a heart-shaped configuration[2] and an azulene-like configuration.[3] Both structures, shown in Figure 1, are based on x-ray results.[2,3] In this paper we discuss the structural possibilities of a ten-membered ring with alternating N, S centers, first in a qualitative manner and then by checking the conclusions with the results of semiempirical calculations.

The structural problem of $S_5N_5^+$ is reminiscent of the structural problem of [10]annulene.[4] In the latter case, research of the past years has shown that the adopted structures can be regarded as resulting from a compromise between a maximum of delocalization of the 10 π electrons (i.e., planarity) and a minimum of angle strain and H···H interaction.

Possible structures which are discussed in the case of [10]annulene are the *all-cis*-[10]annulene **1**, the *cis*^{4},*trans*-[10]annulene **2**, and the *cis*^{3},*trans*^{2}-[10]annulenes **3** and **4**.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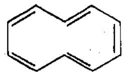
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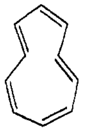
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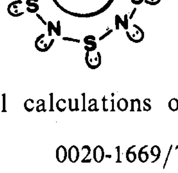
With the assumption of an ideal C–C–C angle of 120°, it is found that the angle strain in planar **1** is a maximum. This explains why **1** is nonplanar and undergoes fast conformational changes via pseudorotation at low temperatures.[4] For **2** a puckered conformer and a less stable, nearly planar conformer have been detected below –40 °C. The electronic spectrum and NMR data are far from those expected for "aromatic" 10π systems. Due to strong H···H repulsions the structures **3** and **4** could only be isolated by replacing internal hydrogens with bridges as in 1,6- or 1,5-methano[10]annulene.[5,6]

Qualitative Discussion

As indicated below, $S_5N_5^+$ is not a 10π system but a 14π system. Nevertheless, the structural problems are similar. A 10π system as well as a 14π system should prefer a planar structure according to the Hückel rule. Instead of the nonbonded H···H interactions in **3** and **4**, we have to worry about the interaction of the lone pairs on the nitrogen and sulfur centers in $S_5N_5^+$.

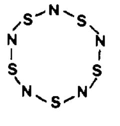
In a localized picture the bonding of $S_5N_5^+$ can be described as follows. The σ skeleton consists of 10 N–S σ bonds; each center is furthermore carrying a "lone pair", n. This makes up for 20 σ and 20 n electrons and leaves 14 π electrons (see below). In this balance the core electrons were omitted.



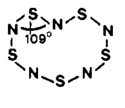
Recent semiempirical calculations on the heart-shaped structure of $S_5N_5^+$ (see Figure 1) confirm this picture.[7] X-ray data from other rings containing $(SN)_x$ fragments indicate[3] that the sulfur centers adopt angles between 90 and 120° while for the nitrogen centers values between 115 and 125° are found. On the average we obtain about the same value as for carbon π systems, namely, 120°. Taking angle strain and lone-pair interactions into account, it is hard to understand why a heart-shaped structure should be preferred over the other ones.

All-Valence-Electron Calculations

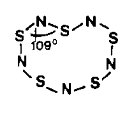
To put the above qualitative discussion for the different structural possibilities on a more quantitative basis we have carried out molecular orbital calculations. We started out with a regular 10-perimeter **1′** (D_{5h}) by adopting equal bond lengths (N–S = 1.56 Å) and bond angles at the nitrogen and sulfur centers of 144°. The other structures were derived from **1** by simple inflections of the perimeter, keeping the bond lengths constant. For the heart-shaped structure as well as for the azulene-like structure two possibilities have been considered (**2′**, **2″** and **4′**, **4″**, respectively). The bond angles were kept at 144° except for those indicated in the formulas.



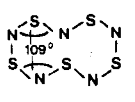
1′(D_{5h})



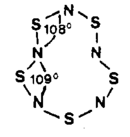
2′(C_{2v})



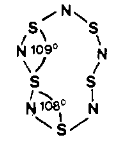
2″(C_{2v})



3′(C_{2v})



4′(C_{2v})



4″(C_{2v})

To estimate the relative energies of these conformers we have carried out all-valence-electron calculations of the extended Hückel (EH) type.[8] Although this method shows numerous deficiencies, it seems to capture the essence of energy changes which accompany variations of bond angles. In the case of the related S_4N_4 problem the EH method predicts essentially the correct bond angles.[9] We did not include 3d basis functions for sulfur since our experience[9] has shown that they can safely be neglected on this level of sophistication. The CNDO/2 method suitable for minimizing the energy with respect to all geometrical parameters proved to be of little use because of convergence problems.

The total energies obtained from the EH calculations are given in Table I. In Figure 2 the total energies are shown as a function of δ, the number of reduced angles, taking the geometry of **1′** as standard. This clearly demonstrates that the reduction of the N–S–N angle from 144 to 109° reduces the total energy while the same reduction of the S–N–S angle raises the energy by about the same amount. In the case of **2′** and **4′** we also calculated the total energy by adopting the structural parameters reported in the literature.[2,3] It should

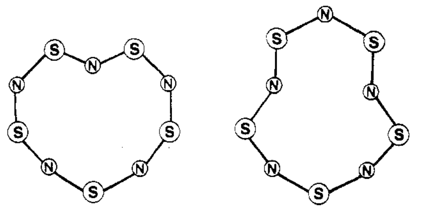


Figure 1. Reported structures of $S_5N_5^+$.

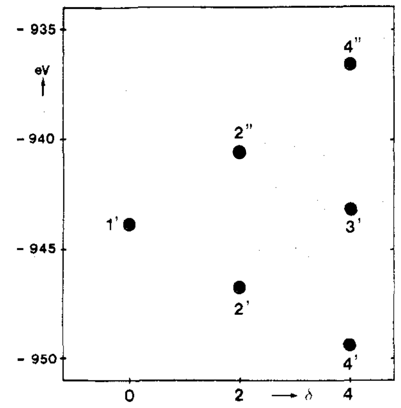


Figure 2. Total energies for **1'** to **4''** as a function of δ, the number of N–S–N or S–N–S angles reduced from 144 to 109°.

Table I. Comparison between the Calculated Total Energies for $S_5N_5^+$ with the Model Structures 1' to 4''

Structure	Energy, eV	Structure	Energy, eV
1'	−943.90	3'	−943.29
2'	−946.75	4'	−949.40
2'[a]	−948.17	4'[a]	−950.25
2''	−940.63	4''	−936.68

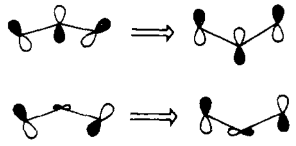
[a] The geometrical parameters reported in the literature have been adopted.

be noted that these energy values can only be considered as rough estimates since bond lengths and angles were not optimized. The pronounced trend of the energy differences we consider to be significant, however.

Discussion of the MO Results

The obtained energy differences may be rationalized by comparison of the predicted MO's for the different structures. It turns out that the energy of the π orbitals changes only slightly by carrying out the variations of the angles. This result is anticipated since the interaction between neighboring p_π AO's does not change by altering the angles and leaving the bond distances constant.

The predicted total energy differences are due primarily to relatively large changes of the orbital energies of the "lone pair" combinations. It should be kept in mind that all ten possible lone-pair combinations are occupied; only the highest ones are shown in Figures 3 and 4. The changes observed can be traced back to two effects: (1) increase of bonding character between neighboring centers as indicated below and (2) bonding or antibonding interactions across the ring.



In Figure 3 we have compared the highest occupied σ orbitals and lowest unoccupied π orbitals of **1'** with those of **4'** and **4''**. In going from **1'** to **4''** there is a dramatic change

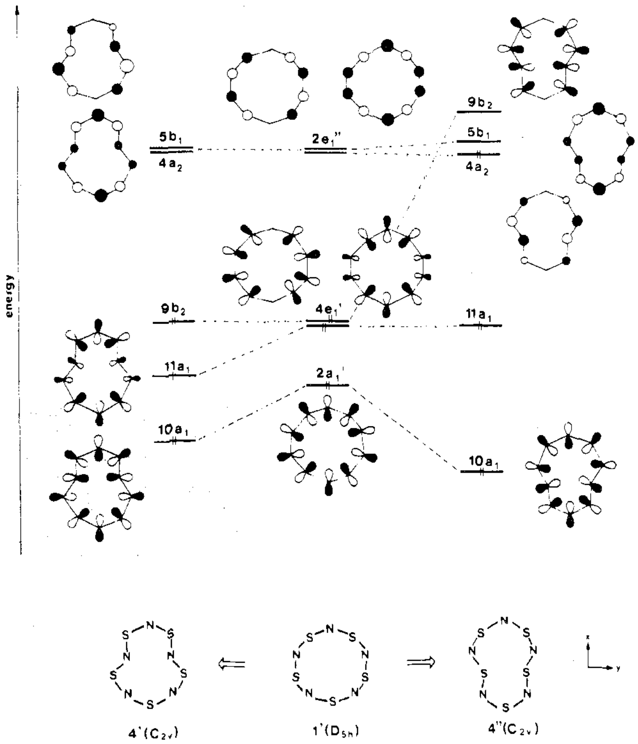
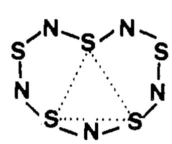


Figure 3. Comparison of the highest occupied σ MO's and lowest unoccupied π MO's of **1'** with those of **4'** and **4''**. The numbering refers to the valence orbitals only.

concerning the orbital energy of the symmetrical 4e' orbital of **1'**. It correlates with $9b_2$ of **4''** and crosses empty π* orbitals. As a result of this the 14π system of **1'** is changed into a 16π system of **4''**. The strong destabilization outweighs the stabilization of the $2a_1'$ orbital.

The change in orbital energies in going from **1'** to the other isomer, **4'**, is a stabilization of the symmetrical 4e' and the $2a_1'$ orbitals of **1'**. The main difference between **4'** and **4''** is due to the fact that the transannular overlap between the p_σ orbitals is about 5 times smaller in the case of nitrogen (**4'**) than in the case of sulfur (**4''**).[9]

In Figure 4 an analogous comparison is made between **1**, **2'**, and **3'**. In going from **1'** to **2'** the increase of bonding character between neighbors dominates. In the case of **3'** this effect is overruled by the antibonding transannular interaction between the lone pairs on N and S which shows up in the destabilization of the $2a_1'$ and the symmetrical combination of the $4e_1'$ orbitals of **1'**. A comparison between the MO's of **2'** and **2''** reveals that in **2''** the antibonding interaction between the sulfur centers, 1, 5, and 7 dominates as indicated below.



Remarks on the Electronic Spectrum of $S_5N_5^+$

The electronic spectrum of $S_5N_5^+$ has been reported.[10] It exhibits a weak band (A) at 24 000 cm^{-1}, an intense band (B) at 30 000 cm^{-1}, and a broad, weak band (C) around 37 000 cm^{-1}. These three bands were interpreted using a π model based on structure **2'** only. PPP–CI calculations were carried out, and band A was assigned to two weakly allowed transitions, while for the region around 30 000 cm^{-1} (band B) four transitions were predicted.

We have investigated the first electronic transitions (π* ← π) as a function of the six structures discussed above. The calculations were based on the PPP–CI model[11] and the

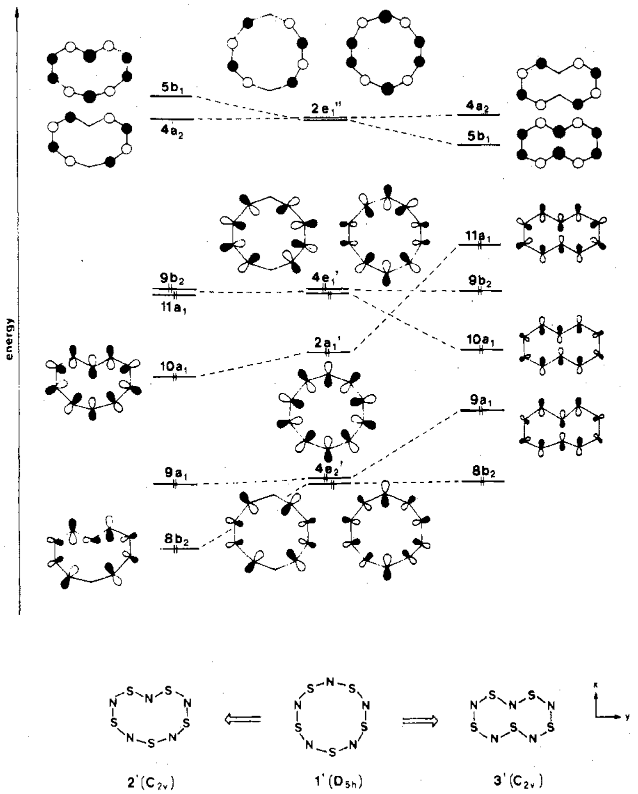


Figure 4. Comparison of the highest occupied σ MO's and lowest unoccupied π MO's of **1'** with those of **2'** and **3'**. The numbering refers to the valence orbitals only.

parameters (method I) suggested by Zahradník et al.[10]

We find only a small difference between the calculated transitions for the various model structures. This is anticipated since all six structures posess the same topology. In our all-valence-electron calculation a lone-pair combination is predicted to be the highest occupied molecular orbital for all six structures. This suggests the possibility that a $\pi^* \leftarrow n$ transition is contributing to one of the first two bands.

Concluding Remarks

Our MO calculations carried out on the six different structural possibilities **1'** to **4''** for $S_5N_5^+$ suggest that the configuration **4'** is a minimum on the $S_5N_5^+$ manifold. This structure provides a minimum of lone-pair interactions together with planarity of the system. The other structures investigated are at most local minima. This result suggests that a careful reexamination of the experimental x-ray data should clarify the question of the existence of two stable conformations of $S_5N_5^+$.

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Reaction Mechanisms of Metal–Metal Bonded Carbonyls. 18.[1] Kinetic Measurement of the Strengths of Some Metal–Metal Bonds

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The kinetics of some reactions in decalin of several substituted dimanganese carbonyl complexes have been studied. Activation enthalpies have been assigned to homolytic fission of the Mn–Mn bonds and provide a kinetic measure of the strengths of these bonds. Electronic absorption spectra of these and some related dimetal carbonyls are reported, and bands corresponding to the excitation of an electron from the metal–metal σ-bonding orbitals to the corresponding antibonding orbitals have been assigned. The effects of substituents on these transitions are interpreted in terms of a strengthening of the metal–metal interactions associated with increasing σ-donor character, increasing π acidity, and decreasing size of the substituents. A linear correlation is found between the activation enthalpies for homolytic fission and the values $h\nu(\sigma \rightarrow \sigma^*)$ for the decacarbonyls and several dimanganese carbonyls with one axial substituent or with two smaller ones. However, activation enthalpies for dimanganese complexes containing larger substituents lie below the linear plot by amounts directly related to the cone angles of the substituents. This is interpreted in terms of a substantial residual steric weakening effect on the kinetic bond strengths over and above the steric effect on the Mn–Mn σ interaction.

Introduction

The strengths of transition metal–transition metal bonds have been a matter of interest ever since the determination of the length of the Mn–Mn bond in $Mn_2(CO)_{10}$ suggested that the Mn–Mn bond was weak.[2] Subsequent thermochemical studies[3] have been undertaken in an attempt to provide quantitative measurement of the strengths of such bonds, but bond energies obtained in this way depend on a