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The Spectra and Bonding of the Thiotrithiazyl Cation, $S_4N_3^+$

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Received June 15, 1965

The planar structure and short, equal sulfur–nitrogen bond lengths of the thiotrithiazyl ($S_4N_3^+$) cation suggest that considerable π bonding occurs in this ring system. Support for this hypothesis is obtained from an examination of the electronic spectra of the thiotrithiazyl cation in concentrated acid media. A model is proposed for the bonding involving a ten-electron π system delocalized over all of the sulfur–nitrogen linkages. The importance of sulfur d orbital participation in the π system is discussed.

Introduction

The recently completed structure determination[1,2] of thiotrithiazyl nitrate, $S_4N_3NO_3$, showed the $S_4N_3^+$ cation to be a planar ring as shown in Figure 1. The most significant features of this structure are the ring planarity, the S–N–S angles, and the S–N distances. Since none of these parameters is predetermined insofar as the establishment of a ring system is concerned, each can be taken as significant reflections of the bonding arrangement.

No other cyclic sulfur–nitrogen system has been found to be planar. Structural investigations have been made for S_4N_4,[3] $S_4N_4H_4$,[4] $S_4N_4F_4$,[5] $S_3N_3Cl_3$,[6] and $S_3N_3O_3Cl_3$.[7] In S_4N_4 the structure is that of a square-planar arrangement of the nitrogen atoms surrounded by a tetrahedral arrangement of the sulfur atoms, and for the six-membered rings the ring is in a "chair" form. The S–N framework in $S_4N_4F_4$ is similar to that of the "tub" form of cyclooctatetraene. The S–N–S bond angles in sulfur nitride are 113°, and in the other molecules they are 122–124°, as compared to the values of 153 and 134° for the $S_4N_3^+$ ring. The average S–N bond length of 1.55 Å. for $S_4N_3^+$ is equal to the shortest S–N ring distances previously known; S_4N_4, by comparison, has average S–N distances of 1.63 Å.

The combination of relatively short and equal N–S bonds, unusually large bond angles at the nitrogen atoms, and ring planarity, coupled with the remarkable stability of the thiotrithiazyl ion toward attack by oxidizing acids (*e.g.*, $S_4N_3NO_3$ can be recrystallized from concentrated nitric acid or aqua regia) suggests the presence of unique bonding in this cyclic system. In this paper we will show that the electronic spectra of $S_4N_3^+$ and some qualitative bonding calculations for this cation support the idea of delocalized molecular orbitals in the ring.

Experimental

Thiotrithiazyl chloride was prepared from the reaction of acetyl chloride with sulfur nitride, as described by MacDiarmid.[8] Ultraviolet and visible spectra of mulls and solutions were obtained with a Beckman DK-1 recording spectrophotometer using quartz cells with 1-cm. path length. Since the only known solvents for salts of the thiotrithiazyl cation are concentrated acids, the spectra were obtained in these solvents. The spectra of freshly prepared solutions obeyed Beer's law; however, solutions which were open to the air for extended periods of time gave evidence of partial decomposition.

The Hückel molecular orbital calculations were done using the University of Arkasas IBM 7040 Computing Center's facilities.

Results

The electronic spectra of the $S_4N_3^+$ cation in 12 *M* HCl, 18 *M* H_2SO_4, and 12 *M* $HClO_4$ media show two peaks in each case at 3420 and 2700 Å, 3320 and 2600 Å., and 3340 and 2580 Å., respectively. In 16 *M* HNO_3 and 15 *M* H_3PO_4 the lower wave length absorption peak is obscured by solvent absorption; and the higher wave length peak was observed at 3400 and 3370 Å., respectively. Mull spectra were obtained to verify that the solution species were essentially the same as those present in the solid. The mull bands are more diffuse; however, the band centers (estimated visually) occur at 3300 and 2650 Å., in agreement with the solution spectra. There is evidence for an additional weak absorption band at *ca.* 3150 Å. which is not observed in the solution spectra. Spectra of $S_4N_3^+$ in sulfuric acid and hydrochloric acid solutions are shown in Figure 2.

Discussion

(A) Electronic Spectra.—The symmetry of $S_4N_3^+$ is nearly C_{2v} and the electronic spectra will be discussed under the selection rules for this symmetry. Of the symmetry allowed transitions ($a_1 \leftrightarrow b_1$ or b_2; $a_2 \leftrightarrow b_1$, b_2), the $\pi \rightarrow \pi^*$ transitions are expected to be more intense than the $n \rightarrow \pi^*$ transitions. This difference in intensities is expected because only the s character of the lone-pair orbitals will give nonzero contributions to the transition moment for the $n \rightarrow \pi^*$ transition.[9a]

The oscillator strengths of the absorption bands were calculated assuming isolated transitions.[9b] The ob-

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[7] A. J. Banister and A. C. Hazell, *ibid.*, 282 (1962).

[8] A. MacDiarmid, *J. Am. Chem. Soc.*, **78**, 3871 (1956).

[9] (a) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 6; (b) T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 277.

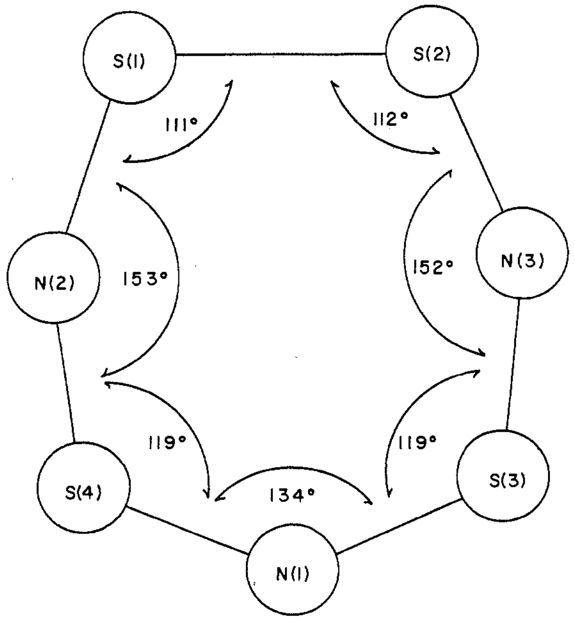

Figure 1.—The planar $S_4N_3^+$ ring. All the N–S bonds are 1.54 ± 0.04 Å., and the S–S bond is 2.06 Å.

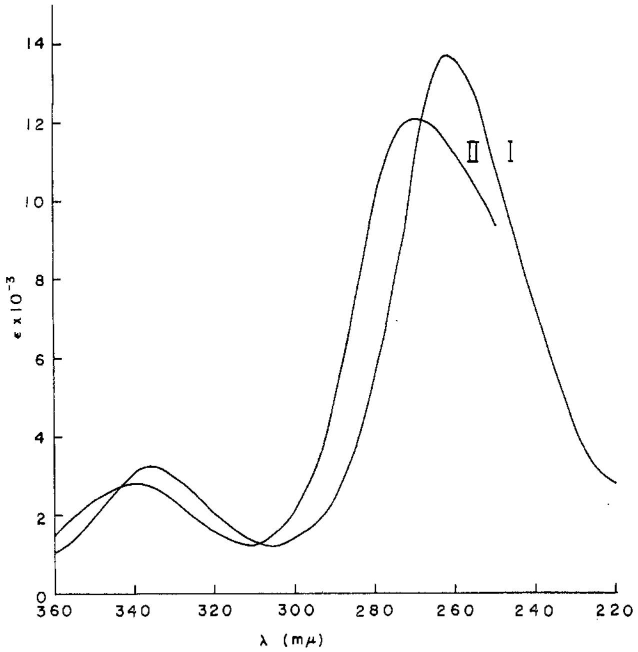

Figure 2.—Absorption spectrum of $S_4N_3^+$ in acid media: curve I, $S_4N_3^+$ in 18 *M* H_2SO_4; curve II, $S_4N_3^+$ in 12 *M* HCl.

served values for the bands at *ca.* 3400 and 2700 Å. were $f = 4.9 \times 10^{-2}$ and $f = 41 \times 10^{-2}$, respectively, in sulfuric acid and $f = 5.1 \times 10^{-2}$ and $f = 40 \times 10^{-2}$ in hydrochloric acid. The assignment of these bands to $\pi \rightarrow \pi^*$ transitions is made on the basis of the high oscillator strengths, the Beer's law dependence, and the concerted shifts observed with a change in solvent; however, these assignments must be treated as provisional in the absence of further data such as polarized spectra. The colors of the salts S_4N_3X ($X = Cl^-$, Br^-, I^-)[8] suggest that charge-transfer bands of the type found for the pyridinium halides[10] may be important for the more easily oxidized halides in the solid state; however, no evidence for such transitions was found for the solution spectra. The weak absorption observed in the mull spectra is not assigned and may be $n \rightarrow \pi^*$; attempts to verify the presence of this band using pressed KBr disks were unsuccessful due to the decomposition of the sample.

(B) **General Bonding Considerations.**—The average N–S bond distance of 1.55 Å. corresponds to a bond order of 2.0 according to a N–S bond order *vs.* bond length correlation presented by Chapman and Waddington.[11] This high bond order all around a planar system strongly suggests a well-developed delocalized π-electron system.

The total number of electrons in the valence shells of the atoms making up the molecule is 38. Fourteen electrons are required for the σ-bonding system of the ring.

Maximum orbital overlap is produced in the σ-bonding framework by assuming sp^2 hybridization for all atoms except for N_2 and N_3, which are assumed to have sp hybridization. There remain unshared electron pairs in sp^2 orbitals on all atoms except N_2 and N_3; for these atoms the lone pairs are considered to be in nearly "pure" p orbitals which are in the plane of the ring. This leaves a p orbital (arbitrarily the p_z) on each atom perpendicular to the plane of the ring; these orbitals are used for the π system of the ring and accommodate the remaining ten electrons. Although this hybridization approach is meant to represent only the most simple working model, it can be noted that any representation of the atom hybridizations by simple hybrids of s and p orbitals necessarily gives "bent" σ bonds, and the scheme used here minimizes the bond bending. The distortion energy lost through inefficient overlap of the σ-bond system can presumably be regained from favorable π interactions.

The assignment of ten electrons to the π system, as outlined in the above model, requires that d orbitals from the sulfur participate in the π system, since ten electrons in a π system composed of p orbitals requires the use of antibonding molecular orbitals.

The most apparent alternate to the above model is the consideration of a six-electron p–π system similar to the tropylium ion. This can be done by assuming sp^3 hybridization for S_1 and S_2, and therefore two nonbonding pairs of electrons for each of these atoms. This reduces the orbital overlap in the S–N σ bonds involving these sulfurs and removes two p orbitals from the π system. However, a major difficulty develops concerning the bond orders of the bonds S_1–N_2 and S_2–N_3. The bond lengths indicate that these are double bonds, while this proposal results in only a single bond. Participation of d orbitals from S_1 and S_2 in the p orbital π system may be proposed to alleviate this difficulty. However, our Hückel molecular orbital calculations indicate that in order to have an appreciable increase in the S_1–N_2 and S_2–N_3 bond orders (from

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(10) E. M. Kosower and P. E. Klinedinst, Jr., *J. Am. Chem. Soc.*, **78**, 3493 (1956).

(11) D. Chapman and T. C. Waddington, *Trans. Faraday Soc.*, **58**, 1679 (1962).

1.00 to 1.64) negative charges of 0.35e must be built up on S_1 and S_2; this charge seems unrealistic to us.

(C) Free Electron Calculations.—Additional support for a ten-electron π system is given by free-electron calculations. Experience with aromatic and conjugated hydrocarbons[9] has indicated that where a delocalized system exists a free-electron model gives a reasonable first approximation to the π–π^* transition energies. In testing the free electron model for $S_4N_3^+$ the familiar equation for a particle in a box, $E_n = n^2h^2/8ml^2$, was used. Since the S_1–S_2 bond has a distance equal to that normally accepted for a single S–S bond, we assume that the π system does not bridge these two atoms. If the length of the box is taken as the sum of the bond lengths around the ring from S_1 to S_2 (a length of 9.3 Å.), ten electrons in the π system puts the first transition (from the $n = 5$ to the $n = 6$ level) at a wave length of 2600 Å. If the box is taken as the sum of the bond lengths from S_1 to S_2 plus an allowance of one-half the S–N distance for extensions of the box beyond these sulfurs (a total length of 10.8 Å.), the first transition is at 3500 Å. The data indicate that the lowest energy π–π^* transition is within this 2600–3500 Å. range. Using six electrons rather than ten with these box lengths gives a first transition range from 4100 to 5500 Å., which is not consistent with the observed bands.

(D) Utilization of Sulfur d Orbitals.—The π-electron system including the contribution of sulfur d orbitals may be treated qualitatively by the methods introduced by Mullikin.[12] Using one p_z orbital from each atom in a Hückel calculation with $\alpha_N = \alpha + 0.5\beta$, $\alpha_s = \alpha + \beta$, and all β's equal, the orbital energies shown as χ_1 to χ_7 in Figure 3 were obtained. The symbols here have their usual significance.[13] The Coulomb integrals were chosen in accord with the atom electronegativities (2.5 for S and 3.0 for N) and the number of electrons contributed to the π system, as suggested by Streitwieser.[13]

The symmetry classification under the C_{2v} group for each orbital is given in Figure 3. With the z axis of each atom perpendicular to the plane of the molecule, the d_{xz} and d_{yz} orbitals have the appropriate symmetry to combine with the orbitals of the π system. Since the orientation of the d orbitals is arbitrary, one of these d orbitals from S_1, labeled S_{d1}, can be assumed to have the orientation required to combine effectively with the π system. The other d orbitals are less desirably oriented and are ignored for the out-of-plane π system. Similar d orbitals from the other sulfur atoms are labeled S_{d2}, S_{d3}, and S_{d4}, where the subscript number refers to the number of the parent sulfur atom. Orbitals S_{d1} and S_{d2} may be combined into symmetry orbitals under the C_{2v} group to form orbital χ_8 of symmetry a_2 and orbital χ_9 of symmetry b_1. Likewise S_{d3} and S_{d4} may be combined to give symmetry orbitals χ_{10} and χ_{11}, of symmetry species a_2 and b_1, respectively. Since the sulfur 3d orbitals are about 8 e.v. above the 3p orbitals, the orbitals χ_8 to χ_{11} are placed in Figure 3 1–2 β units above the sulfur p-orbital energy. These orbitals will interact most strongly with χ_5 and χ_6, which have nearly the same energy. Reasonable expectations for the orbital energies after mixing in the d orbitals are shown as the orbitals labeled ϕ_1 to ϕ_{11} in Figure 3.

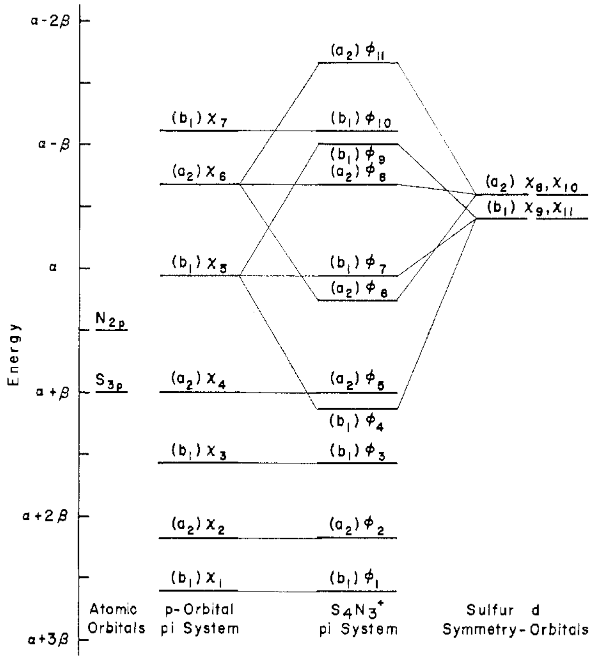

Figure 3.—Orbital energy diagram for $S_4N_3^+$.

Certainly this scheme is approximate and the exact ordering of levels like ϕ_4 and ϕ_5 is unknown. However, our purpose here is not to present detailed calculations but rather to gain a qualitative understanding of how the atomic orbitals can be utilized to produce the rather unique planar $S_4N_3^+$ system. The scheme presented in Figure 3 qualitatively fits the known facts. The ten electrons put into the π system are seen to occupy the five bonding or nonbonding π molecular orbitals. The lowest energy electronic transition at 3400 Å. would be given by a transition from ϕ_5 to ϕ_6. The other bands can also be accounted for on the basis of the orbital levels in Figure 3, but in view of the inexact nature of the level locations there seems to be little point in assigning these at this stage.

In addition to these considerations of π bonding above and below the plane of the ring, π bonds in the plane of the ring are also possible. These overlaps, between the d_{xy} orbitals of the sulfur atoms and the lone pairs of electrons on the nitrogen atoms, have been considered in detail by Craig and Paddock.[14] Whether they are delocalized to any extent or not, they may be of considerable importance in increasing the bond order of the S–N bonds.

Acknowledgment.—The authors wish to acknowledge the helpful comments of a referee.

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