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# <sup>15</sup>N NMR Study of the Oxidation of the Trisulfur Trinitride Anion by Molecular Oxygen: A Comparison of the Molecular and Electronic Structures of the S<sub>3</sub>N<sub>3</sub><sup>-</sup>, S<sub>3</sub>N<sub>3</sub>O<sup>-</sup>, and S<sub>3</sub>N<sub>3</sub>O<sub>2</sub><sup>-</sup> Ions

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The oxidation of the S<sub>3</sub>N<sub>3</sub><sup>-</sup> ion in acetonitrile solution by molecular oxygen gives rise to four major products: S<sub>4</sub>N<sub>5</sub><sup>-</sup>, S<sub>4</sub>N<sub>5</sub>O<sup>-</sup>, S<sub>3</sub>N<sub>3</sub>O<sup>-</sup>, and S<sub>3</sub>N<sub>3</sub>O<sub>2</sub><sup>-</sup>. The relative yields of these species are a function of the flow rate of oxygen, and the progress of the reaction and the structure of the various ions in solution can be analyzed by using <sup>15</sup>N NMR spectroscopy (and <sup>15</sup>N-labeled S<sub>3</sub>N<sub>3</sub><sup>-</sup>). The crystal and molecular structures of (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>S<sub>3</sub>N<sub>3</sub>O<sup>-</sup> and (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>S<sub>3</sub>N<sub>3</sub>O<sub>2</sub><sup>-</sup> have been determined by X-ray diffraction. Crystals of the former are monoclinic, space group *P*<sub>2</sub><sub>1</sub>/*c*, with *a* = 17.161 (2) Å, *b* = 9.970 (1) Å, *c* = 20.591 (2) Å, β = 104.45 (1)°, *V* = 3411.7 Å<sup>3</sup>, and *Z* = 4. Crystals of the latter are monoclinic, space group *P*<sub>2</sub><sub>1</sub>, with *a* = 12.421 (1) Å, *b* = 13.036 (1) Å, *c* = 10.699 (1) Å, β = 103.36 (1)°, *V* = 1685.6 Å<sup>3</sup>, and *Z* = 2. Both structures were solved by direct methods and refined by full-matrix least-squares procedures; for (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>S<sub>3</sub>N<sub>3</sub>O<sup>-</sup> the final *R* = 0.053 and *R*<sub>w</sub> = 0.075 for 3058 reflections with *I* > 3σ(*I*), and for (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>S<sub>3</sub>N<sub>3</sub>O<sub>2</sub><sup>-</sup> the final *R* = 0.048 and *R*<sub>w</sub> = 0.057 for 2312 reflections with *I* > 3σ(*I*). The two anions S<sub>3</sub>N<sub>3</sub>O<sup>-</sup> and S<sub>3</sub>N<sub>3</sub>O<sub>2</sub><sup>-</sup> both possess six-membered S<sub>3</sub>N<sub>3</sub> ring structures with exocyclic oxygen atoms bonded to sulfur (in S<sub>3</sub>N<sub>3</sub>O<sub>2</sub><sup>-</sup> the oxygens are geminally substituted). Both rings exhibit significant variations in chemically equivalent bond lengths and angles. The visible spectra of S<sub>3</sub>N<sub>3</sub>O<sup>-</sup> (λ<sub>max</sub> = 509 and 340 nm) and S<sub>3</sub>N<sub>3</sub>O<sub>2</sub><sup>-</sup> (λ<sub>max</sub> = 562 and 362 nm) are interpreted in terms of the expected perturbations on the π-manifold of the S<sub>3</sub>N<sub>3</sub><sup>-</sup> anion; the observed absorptions are assigned to π\* → π\* type excitations.

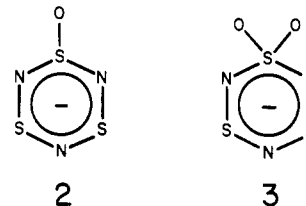
## Introduction

Central to the understanding of the complex and unusual chemistry of sulfur nitride derivatives is the development of a comprehensive theoretical framework for describing their electronic structures. A variety of approaches has been explored, ranging from the empirical rules devised by Banister<sup>2</sup> to the more appealing but still conceptually simple EHMO treatments pioneered by Gleiter.<sup>3</sup> Ab initio molecular orbital calculations on a variety of planar binary species (e.g., S<sub>4</sub>N<sub>4</sub><sup>2+</sup> and S<sub>3</sub>N<sub>3</sub><sup>-</sup>)<sup>4,5</sup> have refined the conclusions of the symmetry-based arguments, while the recent application of the perimeter model to the interpretation of MCD spectra has illustrated the usefulness of simple topological analyses.<sup>6</sup> As a result of this work, the description of the S<sub>3</sub>N<sub>3</sub><sup>-</sup> anion (1) in terms of a fully delocalized six-orbital 10-π-electron system has received both theoretical<sup>5</sup> and experimental<sup>6a</sup> verification.



As a further investigation of the electronic structure of the S<sub>3</sub>N<sub>3</sub><sup>-</sup> system, we are currently exploring its redox properties since, in principle at least, its sequential oxidation could yield S<sub>3</sub>N<sub>3</sub><sup>+</sup> and S<sub>3</sub>N<sub>3</sub><sup>2+</sup>,<sup>5a,8</sup> two species of current theoretical interest

but about which little is known. We report here the results of the oxidation of S<sub>3</sub>N<sub>3</sub><sup>-</sup> with molecular oxygen and illustrate the analysis of the complex mixture of products by using the newly developed <sup>15</sup>N NMR method.<sup>9</sup> The two cyclic oxoanions S<sub>3</sub>N<sub>3</sub>O<sup>-</sup> (2) and S<sub>3</sub>N<sub>3</sub>O<sub>2</sub><sup>-</sup> (3) have been fully characterized by X-ray crystallography (as their (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup> salts), and their molecular and electronic structures are compared with those of their parent S<sub>3</sub>N<sub>3</sub><sup>-</sup> ion.<sup>10</sup>



## Experimental Section

**General Procedures and Instrumentation.** The compounds PPN<sup>+</sup>S<sub>3</sub>N<sub>3</sub><sup>-</sup>,<sup>11</sup> PPN<sup>+</sup>N<sub>3</sub><sup>-</sup>,<sup>12</sup> (PPN<sup>+</sup> = (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>), and S<sub>4</sub>N<sub>4</sub>O<sub>2</sub><sup>13</sup> were

- (1) (a) University of Calgary. (b) University of Arkansas. (c) Permanent address: Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.
- (2) (a) Banister, A. J. *Nature (London), Phys. Sci.* **1972**, *237*, 92. (b) Banister, A. J. *Ibid.* **1972**, *239*, 69.
- (3) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 444.
- (4) (a) Sharma, R. D.; Aubke, F.; Paddock, N. L. *Can. J. Chem.* **1981**, *59*, 3157. (b) Trsic, M.; Laidlaw, W. G.; Oakley, R. T. *Ibid.* **1982**, *60*, 2281. (c) Gillespie, R. J.; Kent, J. P.; Sawyer, J. R.; Slim, D. R.; Tyrer, J. D. *Inorg. Chem.* **1981**, *20*, 3799.
- (5) (a) Bojes, J.; Chivers, T.; Laidlaw, W. G.; Trsic, M. *J. Am. Chem. Soc.* **1979**, *101*, 4517. (b) Chivers, T.; Laidlaw, W. G.; Oakley, R. T.; Trsic, M. *Inorg. Chim. Acta* **1981**, *53*, L189.
- (6) (a) Waluk, J. W.; Michl, J. *Inorg. Chem.* **1981**, *20*, 963. (b) Waluk, J. C.; Chivers, T.; Oakley, R. T.; Michl, J. *Ibid.* **1982**, *21*, 832.

- (7) One-electron oxidation of S<sub>3</sub>N<sub>3</sub><sup>-</sup> to S<sub>3</sub>N<sub>3</sub><sup>•</sup> should strengthen the π-framework of the cyclic structure. However, the direct interconversion of S<sub>3</sub>N<sub>3</sub><sup>-</sup> and (SN)<sub>x</sub> polymer has led to the suggestion that S<sub>3</sub>N<sub>3</sub><sup>-</sup> has an open-chain structure. By contrast, recent PES studies have concluded that S<sub>3</sub>N<sub>3</sub><sup>-</sup> is cyclic. See: (a) Lau, W. M. Ph.D. Thesis, University of British Columbia, 1982. (b) Smith, R. D. *J. Chem. Soc., Dalton Trans.* **1979**, 478. (c) Deutsch, P. W.; Curtiss, L. A. *Chem. Phys. Lett.* **1977**, *51*, 125.
- (8) The preparation of salts of the S<sub>3</sub>N<sub>3</sub><sup>+</sup> cation has been described by several groups, but all these reports have later been retracted or refuted. If it existed as a planar ring, S<sub>3</sub>N<sub>3</sub><sup>+</sup> would possess an open shell diradical configuration.<sup>5a</sup> Cf.: (a) Zborilova, L.; Touzin, J.; Navrátilová, D.; Mikosová, J. *Z. Chem.* **1972**, *12*, 27. (b) Zborilova, L.; Gebauer, P. Z. *Anorg. Allg. Chem.* **1979**, *448*, 5. (c) Banister, A. J.; Padley, J. S. *J. Chem. Soc. A* **1969**, 658. (d) Banister, A. J.; Dainty, P. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2658. (e) Banister, A. J.; Clarke, H. G. *Ibid.* **1972**, 2661. (f) Banister, A. J.; Durant, J. A.; Rayment, I.; Shearer, H. M. M. *Ibid.* **1976**, 928.
- (9) Chivers, T.; Oakley, R. T.; Scherer, O. J.; Wolmershäuser, G. *Inorg. Chem.* **1981**, *20*, 914.
- (10) For a preliminary communication of part of this work, see: Chivers, T.; Oakley, R. T.; Cordes, A. W.; Pennington, W. T. *J. Chem. Soc., Chem. Commun.* **1981**, 1214.
- (11) (a) Chivers, T.; Laidlaw, W. G.; Oakley, R. T.; Trsic, M. *J. Am. Chem. Soc.* **1980**, *102*, 5773. (b) For purposes of identification, PPN<sup>+</sup>S<sub>4</sub>N<sub>4</sub>O<sup>-</sup> was also prepared by cation exchange of PPN<sup>+</sup>Cl<sup>-</sup> with NH<sub>4</sub><sup>+</sup>S<sub>4</sub>N<sub>4</sub>O<sup>-</sup>. See: Steudel, R. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1969**, *24B*, 934.

all prepared according to literature methods. Acetonitrile was purified by distillation from phosphorus pentoxide followed by distillation from calcium hydride. Infrared spectra were recorded on Nujol mulls (CsI windows) on a Perkin-Elmer 467 grating spectrophotometer. UV-visible spectra were recorded on a Cary 219 spectrophotometer, and  $^{15}\text{N}$  NMR spectra were obtained on a Varian XL-200 spectrometer operating at 20.28 MHz. Acquisition parameters were as described elsewhere.<sup>9</sup> All  $^{15}\text{N}$  NMR spectra were run on samples enriched at the 30%  $^{15}\text{N}$  level with  $\text{CH}_2\text{Cl}_2$  as solvent and 0.05 M  $\text{Cr}(\text{acac})_3$  as a PARR,<sup>14</sup> so that pulse delays could be reduced to 3 s. Chemical shifts were measured as previously described<sup>9</sup> and are reported on the  $\delta$  scale with  $\text{NH}_3(\text{l})$  (at 25 °C) as an arbitrary zero point. Chemical shifts relative to  $\text{MeNO}_2$  can be obtained with the relation  $\delta(\text{ref MeNO}_2) = \delta(\text{ref NH}_3(\text{l})) - 380.23 \text{ ppm}$ .<sup>15</sup> Contact shifts due to the PARR were measured to be ca. 1 ppm for  $\text{S}_4\text{N}_5\text{O}^-$  and  $\text{S}_4\text{N}_5^-$  and are expected to be of a similar magnitude for  $\text{S}_3\text{N}_3\text{O}^-$  and  $\text{S}_3\text{N}_3\text{O}_2^-$ . Chemical analyses were performed by MHW Laboratories, Phoenix, AZ.

**Preparation of  $\text{PPN}^+\text{S}_3\text{N}_3\text{O}^-$ .** Dry oxygen was bubbled slowly at a flow rate of ca. 20 mL  $\text{min}^{-1}$  into a stirred solution of  $\text{PPN}^+\text{S}_3\text{N}_3^-$  (2.00 g, 2.9 mmol) in 75 mL of acetonitrile. After 30 min the gas flow was halted, and the deep red solution was left to stand for 1 h. The solution was then concentrated in vacuo to about 15–20 mL, warmed to redissolve some crystalline material that had precipitated, and finally cooled to  $-20^\circ\text{C}$  overnight. The following day two types of crystals were present in the flask: (a) a large quantity of dark red blocks and (b) a smaller quantity of buff-colored needles. The latter material was manually separated from the former and recrystallized from hot acetonitrile as yellow crystalline needles (220 mg). Infrared spectroscopic analysis of these needles showed them to be a mixture of  $\text{PPN}^+\text{S}_4\text{N}_5\text{O}^-$  and  $\text{PPN}^+\text{S}_4\text{N}_5^-$  (each component was identified by comparison of the infrared spectrum of the mixture with those of authentic samples of  $\text{PPN}^+\text{S}_4\text{N}_5\text{O}^-$  and  $\text{PPN}^+\text{S}_4\text{N}_5^-$ ).<sup>11</sup> The deep red crystalline blocks were recrystallized from acetonitrile to give  $\text{PPN}^+\text{S}_3\text{N}_3\text{O}^-$  (870 mg, 1.3 mmol, 42%). Anal. Calcd for  $\text{C}_{36}\text{H}_{30}\text{N}_4\text{O}_2\text{P}_2\text{S}_3$ : C, 62.41; H, 4.36; N, 8.09; S, 13.88. Found: C, 62.11; H, 4.45; N, 8.14; S, 13.64.

**Slow Oxidation of  $\text{PPN}^+\text{S}_3\text{N}_3^-$ .** A slurry of  $\text{PPN}^+\text{S}_3\text{N}_3^-$  (1.00 g, 1.45 mmol) in 15 mL of acetonitrile was allowed to react with atmospheric oxygen by slow diffusion of air through a short ( $\sim 10$  cm)  $\text{CaSO}_4$  drying tube. After 24 h, the deep purple solution was concentrated to ca. 10 mL in vacuo and cooled to  $-20^\circ\text{C}$  overnight. The solution was then filtered to yield 350 mg of buff-colored needles, which were shown by infrared analysis (as above) to be a mixture of  $\text{PPN}^+\text{S}_4\text{N}_5\text{O}^-$  and  $\text{PPN}^+\text{S}_4\text{N}_5^-$ . The deep purple mother liquor was concentrated in vacuo to ca. 5 mL and again cooled to  $-20^\circ\text{C}$  for 24 h. The deep purple crystalline blocks (40 mg) so obtained were identified as  $\text{PPN}^+\text{S}_3\text{N}_3\text{O}_2^-$  by comparison of their infrared spectrum with that of an authentic sample (prepared as described below).

**Preparation of  $\text{PPN}^+\text{S}_3\text{N}_3\text{O}_2^-$ .**<sup>16</sup>  $\text{PPN}^+\text{N}_3^-$  (540 mg, 0.92 mmol) was added as a dry powder to a slurry of  $\text{S}_4\text{N}_4\text{O}_2$  (200 mg, 0.92 mmol) in 20 mL of acetonitrile under an atmosphere of nitrogen. The reaction mixture immediately turned a deep purple color, and  $\text{N}_2$  evolution commenced. The mixture was then stirred and heated to reflux for 3 h. After this time the mixture was cooled to  $-20^\circ\text{C}$  for 2 h, thereby precipitating out a large quantity of deep purple crystals. These crystals were Soxhlet extracted with diethyl ether for 12 h to remove small quantities of  $\text{S}_8$  and then recrystallized from hot acetonitrile to give  $\text{PPN}^+\text{S}_3\text{N}_3\text{O}_2^-$  (513 mg, 0.73 mmol, 79%). Anal. Calcd for  $\text{C}_{36}\text{H}_{30}\text{N}_4\text{O}_2\text{P}_2\text{S}_3$ : C, 61.00; H, 4.27; N, 7.90; S, 13.57. Found: C, 60.30; H, 4.44; N, 7.97; S, 13.16.

**$^{15}\text{N}$  NMR Analysis of the  $\text{S}_3\text{N}_3^-/\text{O}_2$  Reaction.** A 30%  $^{15}\text{N}$ -labeled sample of  $\text{PPN}^+\text{S}_3^*\text{N}_3^-$  ( $\text{S}^* = ^{15}\text{N}$ ) was prepared by the reaction of  $\text{PPN}^+\text{N}_3^-$  with  $\text{S}_4^*\text{N}_4$ .<sup>9</sup> The oxidation of this material by  $\text{O}_2$  yielded

Table I. Crystal Data

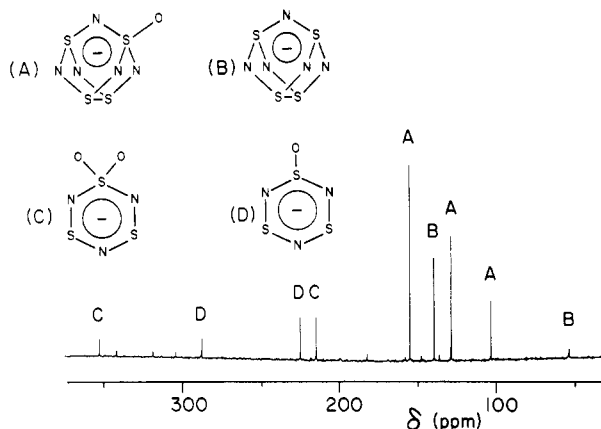
	$\text{PPN}^+\text{S}_3\text{N}_3\text{O}^-$	$\text{PPN}^+\text{S}_3\text{N}_3\text{O}_2^-$
formula	$\text{C}_{36}\text{H}_{30}\text{P}_2\text{N}_4\text{S}_3\text{O}$	$\text{C}_{36}\text{H}_{30}\text{P}_2\text{N}_4\text{S}_3\text{O}_2$
fw	692.82	708.82
space group;	$P2_1/c$ ; 4	$P2_1$ ; 2
molecules/cell		
a, Å	17.161 (2)	12.421 (1)
b, Å	9.970 (1)	13.036 (1)
c, Å	20.591 (2)	10.699 (1)
$\beta$ , deg	104.45 (1)	103.36 (1)
V, Å <sup>3</sup>	3411.7	1685.6
reflens used for unit cell;	16; 50–79	24; 62–85
$2\theta$ range		
calcd density, g cm <sup>-3</sup>	1.35	1.40
reflens scanned; obsd	3775; 3058	2615; 2312
$2\theta$ range of reflens	0–100	0–120
scanned, deg		
$\mu(\text{Cu K}\alpha)$ , cm <sup>-1</sup>	30.7	31.5
range abs cor	0.52–0.68	0.57–0.83
cryst faces; face-to-	(100), (100); 0.153	(100), (100); 0.058
center dist, mm	(102), (102); 0.200	(010), (010); 0.180
	(450), (450); 0.360	(104), (104); 0.270
	(120), 0.380	
	(110), 0.360	
final R; $R_w$	0.053; 0.075	0.048; 0.057
largest shift in final	0.03	0.08
cycle ( $\sigma$ )		
max peak (final diff	0.29	0.39
map), e Å <sup>-3</sup>		
std dev of observn of	0.68	1.86
unit wt		
parameters refined;	418; 7.3	423; 5.5
parameter/reflcn ratio		

the corresponding  $\text{S}_4^*\text{N}_5\text{O}^-$ ,  $\text{S}_4^*\text{N}_5^-$ ,  $\text{S}_3^*\text{N}_3\text{O}^-$ , and  $\text{S}_3^*\text{N}_3\text{O}_2^-$  ions as their  $\text{PPN}^+$  salts. Each of these compounds was individually isolated by fractional crystallization so as to ensure correct assignments of their  $^{15}\text{N}$  NMR signals.

**X-ray Measurements.** The crystal data for  $\text{PPN}^+\text{S}_3\text{N}_3\text{O}^-$  and  $\text{PPN}^+\text{S}_3\text{N}_3\text{O}_2^-$  are given in Table I. Both crystals were sealed under argon in capillary tubes for the X-ray data collection. All measurements were made at 21 °C on a manual GE XRD-5 quarter-circle diffractometer. Periodic measurements of three check reflections showed an X-ray-exposure-dependent decomposition of both crystals with a total intensity loss of 30%. A series of linear corrections adequately compensated for this decay. Both structures were solved with use of the MULTAN80 programs;<sup>17</sup> for the final full-matrix least-squares refinements, the phenyl hydrogen atoms were constrained to idealized positions with  $d(\text{C-H}) = 0.95 \text{ Å}$  and with isotropic thermal parameters of  $B = 5.0 \text{ Å}^2$ . Neutral-atom scattering factors were used for all atoms.<sup>18</sup> The monoxide crystal was found to have 11% of the anion sites occupied by  $\text{S}_3\text{N}_3^-$  in place of  $\text{S}_3\text{N}_3\text{O}^-$ . In the final refinement the S1 and O atoms were given a multiplicity of 0.89, while the "extra" sulfur atom in the plane of the ring atoms had a multiplicity of 0.11 and an isotropic  $B$  of  $7.0 \text{ Å}^2$ . These multiplicities were obtained by refinement of a least-squares calculation at the stage of isotropic thermal parameters and were held at these values for the final anisotropic refinement. The weighting scheme for the monoxide crystal was based on  $\sigma = (2F_{\text{min}} + F_o + 2F_o/F_{\text{max}})$ ,<sup>19</sup> and that of the dioxide was based on counting statistics. Both weighting schemes gave refinements that showed no dependence of  $\Delta F/\sigma$  on either  $F$  or  $\theta$ . The parameter:reflection ratio of 1:5.5 for the  $\text{S}_3\text{N}_3\text{O}_2^-$  crystal was less than ideal, but the anion structural parameters differed by less than  $1\sigma$  from a refinement that employed rigid-group phenyl rings ( $R = 0.068$  for 171 parameters, 1:13.5 parameter:reflection ratio). The hydrogen atom positions, the anisotropic thermal parameters for the non-hydrogen atoms, the distances and angles of the two  $(\text{Ph}_3\text{P})_2\text{N}^+$

- (12) Ruff, J. K.; Schlientz, W. J. *Inorg. Synth.* **1974**, *15*, 84.
- (13) Roesky, H. W.; Schaper, W.; Petersen, O.; Muller, T. *Chem. Ber.* **1977**, *110*, 6952.
- (14) Levy, G. C.; Pakh, T.; Srinivasan, R. P. *Org. Magn. Reson.* **1980**, *14*, 129.
- (15) Levy, G. C.; Lichter, R. L. "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy"; Wiley: New York, 1979.
- (16) The preparation of a tetraalkylammonium salt of the  $\text{S}_3\text{N}_3\text{O}_2^-$  ion via the reaction of azide ion with  $\text{S}_4\text{N}_4\text{O}_2$  was communicated by: Witt, M.; Aramaki, M.; Roesky, H. W., paper presented at the 2nd International Symposium on Inorganic Ring Systems, Gottingen, West Germany, Aug 1978. However, no details have been published.

- (17) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. "MULTAN80" (a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data), University of York, York, England, and University of Louvain, Louvain, Belgium, 1980.
- (18) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol IV.
- (19) Cruickshank, D. W. J. "Crystallographic Computing"; Ahmed, F. H., Ed.; Munksgaard: Copenhagen, 1970; p 195.

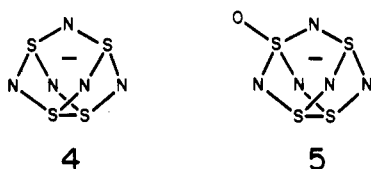


**Figure 1.**  $^{15}\text{N}$  NMR spectrum of a solution of  $\text{PPN}^+\text{S}_3^-\text{N}_3^-$  ( $^*\text{N} = 30\%$   $^{15}\text{N}$ ) in acetonitrile after exposure to dry air for 48 h (0.05 M  $\text{Cr}(\text{acac})_3$  added, 6300 scans, 3-s pulse delay).

cations, and the structure factor tables for both structures have been deposited as supplementary material.

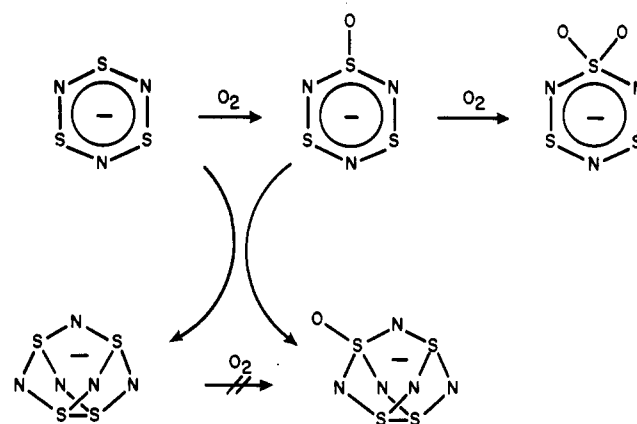
## Results and Discussion

**Oxidation of  $\text{S}_3\text{N}_3^-$  by  $\text{O}_2$ .** The generation of highly colored solutions during the handling of sulfur–nitrogen anions has a long history. Intense colors have been noted during the electrolytic reduction of  $\text{S}_4\text{N}_4$ ,<sup>20</sup> and in hindsight their formation probably stems from the oxidation of the initially produced  $\text{S}_3\text{N}_3^-$ . Red and violet materials have also been reported as a result of treating the red isomer of thionylimide HNSO with organolithium reagents.<sup>21</sup> These latter derivatives have never been properly characterized, but their color and mode of preparation again suggest a connection to the products obtained via the air oxidation of  $\text{S}_3\text{N}_3^-$ .<sup>21c</sup> When exposed to the atmosphere, solutions of the  $\text{S}_3\text{N}_3^-$  ion in acetonitrile turn from yellow to red and eventually to purple. Preliminary analysis of these oxidized solutions indicated a complex mixture of products. The presence of the well-known  $\text{S}_4\text{N}_5^-$  (4) and  $\text{S}_4\text{N}_5\text{O}^-$  (5) species was readily detected by infrared analysis, but neither of these ions account for the intense red and purple colors being produced (both the  $\text{S}_4\text{N}_5^-$  and  $\text{S}_4\text{N}_5\text{O}^-$  ions are yellow).



In order to probe the course of the oxidation more carefully, we have utilized the newly developed technique of  $^{15}\text{N}$  NMR spectroscopy on  $^{15}\text{N}$ -enriched  $\text{S}_3\text{N}_3^-$ .<sup>9</sup> Figure 1 illustrates the  $^{15}\text{N}$  NMR spectrum of a typical mixture obtained by allowing a solution of  $\text{PPN}^+\text{S}_3^-\text{N}_3^-$  ( $^*\text{N} = 30\%$   $^{15}\text{N}$ ) to oxidize slowly by diffusion of dry air through a short capillary tube. Under such conditions the cage anions  $\text{S}_4\text{N}_5^-$  and  $\text{S}_4\text{N}_5\text{O}^-$  are the major products. However, other signals to low field of the cage species are also observed, and by careful fractional crystallization the two components responsible for these signals can be isolated. One is the novel monooxanion  $\text{S}_3\text{N}_3\text{O}^-$  (2), which is presumably the initial oxidation product of  $\text{S}_3\text{N}_3^-$ . The

Scheme I



**Table II.**  $^{15}\text{N}$  Chemical Shifts of Products Obtained from  $\text{O}_2$  Oxidation of  $\text{S}_3\text{N}_3^-$

anion	$\delta^a$
$\text{S}_4\text{N}_5^-$	139.7 (4 N), 54.3 (1 N)
$\text{S}_4\text{N}_5\text{O}^-$	147.9 (2 N), 129.0 (2 N), 104.0 (1 N)
$\text{S}_3\text{N}_3\text{O}^-$	288.3 (1 N), 225.4 (2 N)
$\text{S}_3\text{N}_3\text{O}_2^-$	353.3 (1 N), 215.2 (2 N)

<sup>a</sup>  $\delta$  ( $\text{CH}_2\text{Cl}_2$ , 0.05 M  $\text{Cr}(\text{acac})_3$  added) reference  $\text{NH}_3(\text{l})$  at  $25^\circ\text{C}$ .

second species is the dioxanion  $\text{S}_3\text{N}_3\text{O}_2^-$  (3), a compound that was recently reported as the product of the reaction of azide ion with  $\text{S}_4\text{N}_4\text{O}_2$ .<sup>16</sup>

The formation of the four ions  $\text{S}_4\text{N}_5^-$ ,  $\text{S}_4\text{N}_5\text{O}^-$ ,  $\text{S}_3\text{N}_3\text{O}^-$ , and  $\text{S}_3\text{N}_3\text{O}_2^-$  during the oxidation of  $\text{S}_3\text{N}_3^-$  poses several interesting and perplexing mechanistic questions (see Scheme I). The rate of oxidation of  $\text{S}_3\text{N}_3^-$  to  $\text{S}_3\text{N}_3\text{O}^-$  is considerably faster than that of  $\text{S}_3\text{N}_3\text{O}^-$  to  $\text{S}_3\text{N}_3\text{O}_2^-$ , and moderate yields of  $\text{S}_3\text{N}_3\text{O}^-$  can be obtained ( $\sim 40\%$ ) with a suitably controlled flow rate of oxygen (see Experimental Section). However, the principal cause of  $\text{S}_3\text{N}_3\text{O}^-$  depletion is not further oxygenation but rather the production of the cage species  $\text{S}_4\text{N}_5^-$  and  $\text{S}_4\text{N}_5\text{O}^-$ . In this context it should also be noted that neither the  $\text{S}_3\text{N}_3\text{O}^-$  ion nor the  $\text{S}_4\text{N}_5^-$  ion are (by themselves) oxidized to  $\text{S}_4\text{N}_5\text{O}^-$ . In a purely formal sense the  $\text{S}_4\text{N}_5^-$  and  $\text{S}_4\text{N}_5\text{O}^-$  ions can be viewed as the products of an addition of an NSN fragment to either  $\text{S}_3\text{N}_3^-$  or  $\text{S}_3\text{N}_3\text{O}^-$  (in the latter case a structural isomerization must also occur<sup>22</sup>). The transfer of an NSN moiety<sup>23a</sup> from one molecule to another is not without precedent; e.g., the reaction of  $\text{S}_3\text{N}_3^-$  with  $\text{S}_4\text{N}_4$  produces  $\text{S}_4\text{N}_5^-$ .<sup>20a</sup> In the present case the origin of the NSN fragment is unknown. It would appear that the formation of  $\text{S}_4\text{N}_5^-$  and  $\text{S}_4\text{N}_5\text{O}^-$  requires the combined interaction of  $\text{S}_3\text{N}_3^-$ ,  $\text{S}_3\text{N}_3\text{O}^-$ , and (perhaps) oxygen, but the nature of the reaction is unknown. A more detailed examination of this process is under way.

**$^{15}\text{N}$  NMR Spectra of Products.** The chemical shift data for the ions discussed in this paper are provided in Table II. For two species,  $\text{S}_3\text{N}_3^-$  and  $\text{S}_4\text{N}_5^-$ ,  $^{15}\text{N}$  NMR shifts have already been reported.<sup>9</sup> For the latter, the 4:1 intensity ratio observed for the two resonances supports the solid-state structural evidence.<sup>24a</sup> Oxidation of one of the bridgehead sulfurs, as in  $\text{S}_4\text{N}_5\text{O}^-$ ,<sup>24b</sup> removes the equivalence of the four cage nitrogens of  $\text{S}_4\text{N}_5^-$ , so that two signals are now observed for the two equivalent pairs of cage nitrogens. The absolute assignment of these two resonances is not possible, but as in  $\text{S}_4\text{N}_5^-$  itself, both signals are to low field of the bridgehead nitrogen (in agreement with charge density calculations<sup>25</sup>). Consistent

- (20) (a) Bojes, J.; Chivers, T.; Drummond, I.; MacLean, G. *Inorg. Chem.* **1978**, *17*, 3668. (b) Bojes, J.; Chivers, T. *Ibid.* **1978**, *17*, 318. (c) Williford, J. D.; Van Reet, R. E.; Eastman, M. P.; Prater, K. B. *J. Electrochem. Soc.* **1973**, *120*, 1498.
- (21) (a) Becke-Goehring, M.; Schwarz, R.; Spiess, W. Z. *Anorg. Allg. Chem.* **1958**, *293*, 294. (b) Goehring, M.; Messner, J. *Ibid.* **1952**, *268*, 47. (c) Heal, H. G. "The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus"; Academic Press: London, 1980; p 49.

- (22) Bartetzko, R.; Gleiter, R. *Chem. Ber.* **1980**, *113*, 1138.

- (23) Laidlaw, W. G.; Trsic, M. *Inorg. Chem.* **1981**, *20*, 1792.

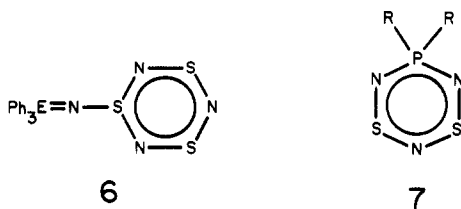
- (24) (a) Flues, W.; Scherer, O. J.; Weiss, J.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 379. (b) Luger, P.; Bradaczek, H.; Steudel, R. *Chem. Ber.* **1976**, *109*, 3441.

Table III. Fractional Coordinates for (A)  $\text{PPN}^+\text{S}_3\text{N}_3\text{O}^-$  and (B)  $\text{PPN}^+\text{S}_3\text{N}_3\text{O}_2^-$ 

	A			B		
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
S1	0.2852 (1)	0.3279 (2)	0.2283 (1)	0.1423 (1)	0.3711 (1)	0.7165 (2)
S2	0.1881 (1)	0.1681 (2)	0.1299 (1)	-0.0791 (2)	0.3585 (2)	0.6794 (3)
S3	0.3321 (1)	0.0704 (2)	0.2090 (1)	0.0136 (2)	0.5492 (2)	0.7087 (3)
N1	0.2592 (4)	0.0621 (6)	0.1467 (3)	-0.0922 (6)	0.4822 (7)	0.6838 (8)
N2	0.3326 (3)	0.1903 (6)	0.2574 (3)	0.1237 (5)	0.4952 (5)	0.7052 (7)
N3	0.1950 (3)	0.2796 (6)	0.1858 (3)	0.0421 (5)	0.3318 (6)	0.7730 (7)
O1	0.2741 (4)	0.3986 (5)	0.2856 (3)	0.1506 (5)	0.3376 (6)	0.5941 (5)
O2				0.2397 (4)	0.3525 (6)	0.8154 (5)
S1'	0.256 (1)	0.279 (2)	0.2495 (8)			
P1	0.1662 (1)	0.7169 (1)	0.4177 (1)	0.6939 (1)	0.3298 <sup>a</sup>	0.0673 (1)
N4	0.2560 (2)	0.7060 (3)	0.4124 (2)	0.6019 (4)	0.2909 (4)	0.1374 (4)
P2	0.3388 (1)	0.7800 (1)	0.4360 (1)	0.5651 (1)	0.3255 (2)	0.2633 (1)
C1	0.1239 (3)	0.5521 (4)	0.4091 (2)	0.7631 (4)	0.2213 (4)	0.0187 (5)
C2	0.1575 (3)	0.4537 (5)	0.3770 (2)	0.8619 (5)	0.2347 (5)	-0.0215 (6)
C3	0.1231 (3)	0.3271 (5)	0.3671 (3)	0.9145 (6)	0.1510 (6)	-0.0582 (7)
C4	0.0551 (4)	0.3002 (6)	0.3878 (3)	0.8703 (6)	0.0563 (6)	-0.0581 (7)
C5	0.0213 (4)	0.3971 (7)	0.4192 (3)	0.7735 (6)	0.0402 (5)	-0.0201 (7)
C6	0.0544 (3)	0.5238 (5)	0.4294 (3)	0.7194 (5)	0.1237 (5)	0.0196 (6)
C7	0.1555 (2)	0.7815 (4)	0.4961 (2)	0.8006 (5)	0.4088 (5)	0.1642 (5)
C8	0.1895 (3)	0.7093 (4)	0.5540 (2)	0.8813 (5)	0.3626 (5)	0.2584 (6)
C9	0.1895 (3)	0.7569 (6)	0.6163 (3)	0.9600 (5)	0.4242 (9)	0.3388 (7)
C10	0.1557 (3)	0.8798 (7)	0.6218 (3)	0.9568 (7)	0.5288 (8)	0.3250 (9)
C11	0.1205 (4)	0.9522 (6)	0.5659 (3)	0.8772 (7)	0.5741 (6)	0.2319 (8)
C12	0.1207 (3)	0.9047 (5)	0.5022 (2)	0.7990 (5)	0.5150 (5)	0.1505 (6)
C13	0.1074 (2)	0.8217 (4)	0.3531 (2)	0.6330 (4)	0.4005 (4)	-0.0755 (5)
C14	0.1459 (3)	0.9041 (5)	0.3164 (2)	0.5174 (5)	0.4057 (4)	-0.1170 (6)
C15	0.1025 (3)	0.9915 (6)	0.2700 (3)	0.4706 (5)	0.4584 (5)	-0.2314 (7)
C16	0.0201 (4)	0.9990 (6)	0.2592 (3)	0.5372 (6)	0.5058 (5)	-0.2981 (6)
C17	-0.0196 (3)	0.9142 (6)	0.2939 (2)	0.6497 (6)	0.5018 (5)	-0.2599 (6)
C18	0.0241 (3)	0.8288 (5)	0.3410 (2)	0.6975 (5)	0.4484 (5)	-0.1461 (6)
C19	0.3320 (2)	0.9499 (4)	0.4627 (2)	0.6312 (4)	0.2512 (4)	0.4000 (5)
C20	0.3246 (3)	1.0552 (5)	0.4178 (2)	0.6953 (5)	0.1676 (5)	0.3847 (6)
C21	0.3077 (3)	1.1842 (5)	0.4370 (3)	0.7403 (5)	0.1048 (5)	0.4872 (7)
C22	0.2992 (3)	1.2050 (5)	0.5003 (3)	0.7246 (6)	0.1256 (5)	0.6094 (7)
C23	0.3067 (3)	1.1022 (6)	0.5456 (3)	0.6633 (6)	0.2097 (5)	0.6259 (6)
C24	0.3240 (3)	0.9741 (5)	0.5273 (2)	0.6150 (5)	0.2726 (5)	0.5232 (6)
C25	0.3859 (3)	0.7803 (4)	0.3668 (2)	0.5895 (5)	0.4591 (4)	0.3015 (6)
C26	0.3508 (3)	0.7096 (5)	0.3095 (2)	0.6742 (5)	0.4939 (5)	0.4026 (6)
C27	0.3882 (4)	0.7022 (6)	0.2578 (3)	0.6937 (6)	0.5983 (5)	0.4185 (7)
C28	0.4608 (4)	0.7665 (7)	0.2635 (3)	0.6334 (6)	0.6672 (5)	0.3340 (8)
C29	0.4965 (3)	0.8351 (7)	0.3208 (3)	0.5489 (6)	0.6327 (5)	0.2322 (8)
C30	0.4594 (3)	0.8433 (5)	0.3732 (3)	0.5268 (5)	0.5297 (5)	0.2183 (6)
C31	0.4030 (2)	0.6927 (4)	0.5043 (2)	0.4179 (4)	0.3057 (4)	0.2379 (5)
C32	0.3876 (3)	0.5587 (5)	0.5154 (2)	0.3596 (5)	0.2600 (5)	0.1248 (6)
C33	0.4371 (4)	0.4901 (5)	0.5669 (3)	0.2452 (6)	0.2463 (6)	0.1058 (8)
C34	0.5016 (3)	0.5514 (6)	0.6085 (3)	0.1927 (5)	0.2742 (6)	0.1993 (8)
C35	0.5191 (3)	0.6827 (6)	0.5984 (2)	0.2495 (5)	0.3195 (7)	0.3111 (7)
C36	0.4699 (3)	0.7531 (5)	0.5460 (2)	0.3624 (5)	0.3361 (7)	0.3296 (6)

<sup>a</sup> Origin-determining parameter.

with their cyclic structures, the two oxyanions  $\text{S}_3\text{N}_3\text{O}^-$  and  $\text{S}_3\text{N}_3\text{O}_2^-$  both exhibit two-line spectra. Significantly, the chemical shifts of the two types of nitrogen ( $\text{N}_{2,6}$  and  $\text{N}_4$ ) in  $\text{S}_3\text{N}_3\text{O}^-$  are remarkably similar to those found in the formally isoelectronic derivatives  $\text{Ph}_3\text{E}=\text{NS}_3\text{N}_3$  ( $\text{E} = \text{P}, \text{As}$ ) (6).<sup>9</sup>



Likewise, there is a close correspondence between the chemical shifts of the  $\text{N}_{2,6}$  and  $\text{N}_4$  resonances in  $\text{S}_3\text{N}_3\text{O}_2^-$  and those found in the structurally related cyclophosphadithiazene

molecules (7).<sup>25</sup> While the theoretical interpretation of  $^{15}\text{N}$  NMR chemical shifts in sulfur nitride systems is not yet on a firm basis, it is satisfying to note the regularity in chemical shift behavior within a series of molecules with similar molecular and electronic structures. Such observations will undoubtedly assist in the future identification of novel species.

**Molecular Geometries of  $\text{S}_3\text{N}_3\text{O}^-$  and  $\text{S}_3\text{N}_3\text{O}_2^-$ .** The structures of  $\text{PPN}^+\text{S}_3\text{N}_3\text{O}^-$  and  $\text{PPN}^+\text{S}_3\text{N}_3\text{O}_2^-$  both consist of discrete cations and anions; there are no unusually short interionic contacts. Final positional parameters for both structures are presented in Table III, and Table IV gives the bond lengths and valence angles within the two anions. Figure 2 illustrates ORTEP drawings of  $\text{S}_3\text{N}_3\text{O}^-$  and  $\text{S}_3\text{N}_3\text{O}_2^-$ .

The primary structural effect of the oxidation of  $\text{S}_3\text{N}_3^-$  to  $\text{S}_3\text{N}_3\text{O}^-$  is to displace the oxidized sulfur atom (by 0.67 Å) out of the plane of the remaining endocyclic atoms (which are coplanar to within 0.04 Å). Within the approximately planar  $\text{S}_2\text{N}_3$  fragment the bond angles remain comparable to those found in  $\text{S}_3\text{N}_3^-$  ( $115^\circ$  vs.  $117^\circ$  at S,  $124^\circ$  vs.  $123^\circ$  at N), but the S–N distances are, on average, 0.03 Å shorter (1.57 Å vs. 1.60 Å in  $\text{S}_3\text{N}_3^-$ ).<sup>5a</sup> The endocyclic angle at the oxidized sulfur

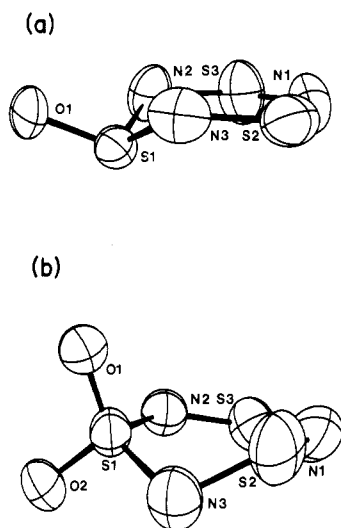
(25) Chivers, T.; Fielding, L.; Laidlaw, W. G.; Trsic, M. *Inorg. Chem.* **1979**, *18*, 3379.

(26) Burford, N.; Chivers, T.; Cordes, A. W.; Laidlaw, W. G.; Noble, M. C.; Oakley, R. T.; Swepston, P. N. *J. Am. Chem. Soc.* **1982**, *104*, 1282.

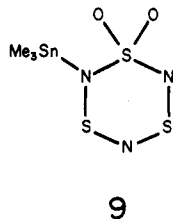
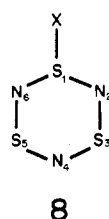
**Table IV.** Distances (Å) and Angles (deg) within the  $S_3N_3O^-$  and  $S_3N_3O_2^-$  Anions<sup>a</sup>

	$S_3N_3O^-$	$S_3N_3O_2^-$
S1-N2	1.632 (6)	1.635 (7)
S1-N3	1.648 (6)	1.589 (7)
S2-N1	1.585 (7)	1.623 (9)
S2-N3	1.584 (7)	1.642 (8)
S3-N1	1.554 (7)	1.549 (9)
S3-N2	1.556 (6)	1.546 (7)
S1-O1	1.428 (6)	1.432 (6)
S1-O2		1.406 (6)
S1'-N2	1.56 (2)	
S1'-N3	1.46 (2)	
N2-S1-N3	105.4 (3)	103.7 (4)
N1-S2-N3	113.3 (3)	106.0 (4)
N1-S3-N2	116.4 (4)	117.3 (4)
S2-N1-S3	124.2 (3)	118.6 (3)
S1-N2-S3	119.2 (1)	124.1 (4)
S1-N3-S2	118.7 (2)	112.9 (1)
N2-S1-O1	105.5 (3)	107.7 (3)
N3-S1-O1	106.3 (3)	105.5 (4)
N2-S1-O2		106.1 (4)
N3-S1-O2		119.1 (4)
O1-S1-O2		113.8 (4)
N2-S1'-N3	119.4 (3)	

<sup>a</sup> Estimated standard deviations of the least significant figure are given in parentheses. The S1' atom is the disordered position of S1 (see text).

**Figure 2.** ORTEP drawings (50% probability ellipsoids) of the  $S_3N_3O^-$  (a) and  $S_3N_3O_2^-$  (b) ions.

atom is more nearly tetrahedral ( $105^\circ$ ), and the mean N-S1 bond distance of 1.64 Å is significantly longer than in  $S_3N_3^-$ . The oxygen ligand lies in a pseudoequatorial orientation with respect to the  $S_3N_3$  ring. Thus, the structure of  $S_3N_3O^-$  closely resembles those of  $Ph_3P=NS_3N_3^{27}$  and  $Ph_3As=NS_3N_3$  (6),<sup>28</sup> with somewhat shorter S-N distances being found in the oxide. Table V provides a comparison of the mean structural parameters of all three  $S_3N_3X$  molecules (8).

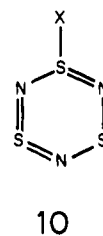
**Table V.** Structural Parameters for  $S_3N_3X$  Derivatives<sup>a</sup>

	$S_3N_3N=PPh_3^b$	$S_3N_3N=AsPh_3^c$	$S_3N_3O^-^d$
Bonds (Å)			
S1-N (av)	1.68 (1)	1.678 (8)	1.640 (8)
S(3,5)-N (av)	1.59 (7)	1.60 (1)	1.57 (1)
Angles (deg)			
N2-S1-N6	109.2 (5)	107.2 (3)	105.4 (3)
S-N(2,6)-S (av)	117.5 (4)	119 (1)	119.0 (3)
S3-N4-S5	127.3 (9)	124.0 (3)	124.2 (3)
N-S-N4 (av)	114.5 (1.8)	115.5 (6)	115 (2)
N-S1-X (av)	104.7 (5)	105.8 (4)	105.9 (4)
NS1N to NSNSN dihedral angle	139	140	137

<sup>a</sup> See structural formula 8 for atom numbering. <sup>b</sup> Reference 27. <sup>c</sup> Reference 28. <sup>d</sup> This report.

In the  $S_3N_3O_2^-$  structure the oxidized sulfur atom forms part of an approximately planar (to within 0.1 Å) five-atom sequence. One of the nitrogen atoms (N3) adjacent to this sulfur atom is displaced 0.80 Å from the best plane. Such a geometry is reminiscent of that observed in the trimethyltin derivative  $Me_3SnS_3N_3O_2$  (9), in which the nitrogen atom bonded to tin is displaced significantly from the plane of the other ring atoms.<sup>29</sup> Accompanying this distortion of the six-membered ring, there is very little regularity in the S-N bond lengths or the endocyclic angles. While the mean angles and bonds associated with the nearly planar part of the ring resemble those found in  $S_3N_3^-$ , the angle at N3 is unusually small ( $112.9^\circ$ ).

The solid-state structures of the two oxyanions  $S_3N_3O^-$  and  $S_3N_3O_2^-$  are, as described above, surprisingly asymmetric. By contrast, the appearance of their  $^{15}N$  NMR spectra indicates a relatively high symmetry (at least  $C_3$ ) in solution. A similar dichotomy is observed in  $S_3N_3^-$  itself; in the solid state the structure of  $Bu_4N^+S_3N_3^-$  exhibits S-N distances ranging from 1.58 (1) to 1.63 (1) Å,<sup>5a</sup> while in solution the three nitrogen atoms give rise to a single sharp  $^{15}N$  resonance, even at  $-80^\circ C$ .<sup>9</sup> The occurrence of lowered symmetry in the solid state is, in fact, a general feature of many structures involving conjugated S-N units. In phosphadithiazines  $R_2PS_2N_3$  (7), the conformation of the ring is markedly dependent on the nature of the exocyclic group R.<sup>26,30</sup> Similarly, in the six-membered ring  $Ph_3P=NS_3N_3^{27}$  (6) there are variations in observed bond lengths that are temptingly reminiscent of valence bond formulations such as 10.<sup>31</sup>



In a molecular orbital context, the distortions observed in all of these structures are a consequence of their electron-rich character. The occupancy of the  $\pi^*$ -orbitals as well as  $\pi$ -orbitals creates a weakened  $\pi$ -framework and leads to a number of low-lying excited states (all of the above compounds display intense low-energy visible absorptions). These features are the classic requirements for pseudo-Jahn-Teller distortions.

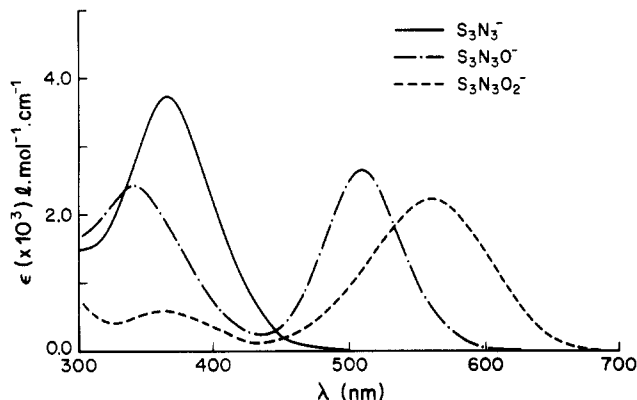
(29) Roesky, H. W.; Witt, M.; Diehl, M.; Bats, J. W.; Fuess, H. *Chem. Ber.* **1979**, *112*, 1372.

(30) Weiss, J. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2272.

(31) Throughout this paper we have depicted molecular structures using delocalized bonds. Although such formulations are open to criticism, they provide a much better representation of the electron distribution than does a single valence-bond model.

(27) Holt, E. M.; Holt, S. L. *J. Chem. Soc., Dalton Trans.* **1974**, 1990.

(28) Holt, E. M.; Holt, S. L.; Watson, K. J. *J. Chem. Soc., Dalton Trans.* **1976**, 54.



**Figure 3.** Visible spectra (in  $\text{CH}_2\text{Cl}_2$  solution) of the  $\text{S}_3\text{N}_3^-$ ,  $\text{S}_3\text{N}_3\text{O}^-$ , and  $\text{S}_3\text{N}_3\text{O}_2^-$  ions.

**Table VI.** Visible Spectra of  $\text{S}_3\text{N}_3^-$ ,  $\text{S}_3\text{N}_3\text{O}^-$ , and  $\text{S}_3\text{N}_3\text{O}_2^-$ <sup>a</sup>

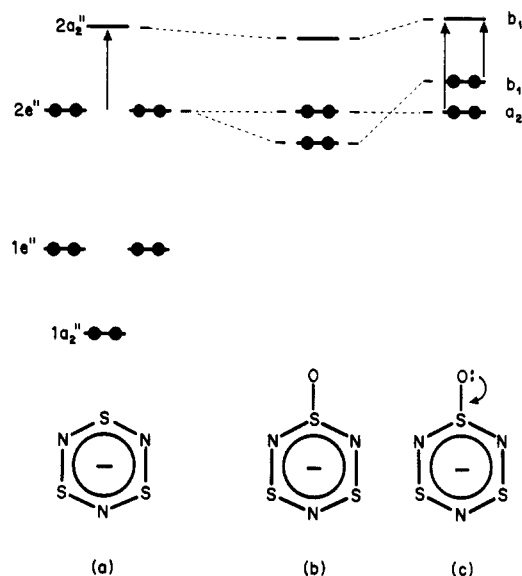
anion	$\lambda_{\text{max}}$ ( $10^{-3}\epsilon$ )	anion	$\lambda_{\text{max}}$ ( $10^{-3}\epsilon$ )
$\text{S}_3\text{N}_3^-$	365 (4)	$\text{S}_3\text{N}_3\text{O}_2^-$	562 (2), 362 (0.5)
$\text{S}_3\text{N}_3\text{O}^-$	509 (3), 340 (2)		

<sup>a</sup> As PPN<sup>+</sup> salts; in  $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{max}}$  in nm,  $\epsilon$  in  $\text{M}^{-1}\text{cm}^{-1}$ .

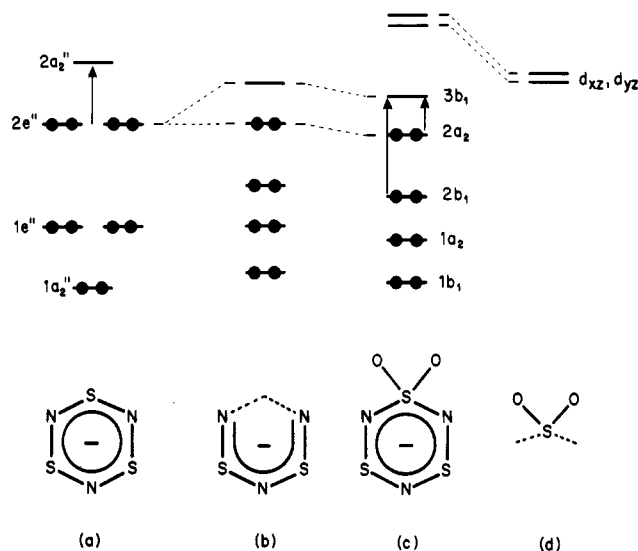
tions.<sup>32,33</sup> The potential for puckering of the  $\text{S}_4\text{N}_4^{2+}$  dication has already been remarked upon by Paddock and co-workers,<sup>4a,c</sup> and in the present case the departure from  $C_s$  symmetry (for  $\text{S}_3\text{N}_3\text{O}^-$ ) and from  $C_{2v}$  symmetry (for  $\text{S}_3\text{N}_3\text{O}_2^-$ ) may also be a manifestation of a particularly low barrier to distortion or, indeed, an unsymmetrical ground state. Either way the rings are likely to be quite flexible, so that lattice forces alone will be sufficient to induce skeletal deformations. In solution such packing effects will be absent, and a higher symmetry is observed (on an NMR time scale).

**Electronic Structures of  $\text{S}_3\text{N}_3^-$ ,  $\text{S}_3\text{N}_3\text{O}^-$ , and  $\text{S}_3\text{N}_3\text{O}_2^-$ .** The most striking physical property of the anions  $\text{S}_3\text{N}_3^-$ ,  $\text{S}_3\text{N}_3\text{O}^-$ , and  $\text{S}_3\text{N}_3\text{O}_2^-$  is the intense visible absorptions that they display. Solutions of the three anions are yellow, burgundy red, and purple, respectively; Figure 3 illustrates their visible spectra, and Table VI provides  $\lambda_{\text{max}}$  and extinction coefficient values. In the case of  $\text{S}_3\text{N}_3^-$ , the description of its electronic structure in terms of a delocalized 10- $\pi$ -electron system is well established<sup>5,6</sup> and a qualitative understanding of the electronic structures and spectra of its two oxyanion derivatives can be conveniently developed in terms of the expected perturbations of the  $\pi$ -manifold of the parent ion.<sup>34</sup>

For the  $\text{S}_3\text{N}_3\text{O}^-$  ion we can begin by considering the effects on the  $\text{S}_3\text{N}_3^-$   $\pi$ -system brought about by the addition of an oxygen ligand to one sulfur. There are two factors to be considered: (a) the increase in the formal oxidation state of the substituted sulfur will increase the effective electronegativity of the  $\pi$ -type lone pair remaining on this sulfur and (b) the exocyclic oxygen (which is a strong  $\pi$ -donor) can interact conjugatively with the ring  $\pi$ -system. The consequences of these two perturbations on the frontier MO's of  $\text{S}_3\text{N}_3^-$  are illustrated schematically in Figure 4. Regardless of the relative magnitude of the two effects, their net result will be a splitting of the degenerate HOMO pair  $2e''$  of  $\text{S}_3\text{N}_3^-$  (one of these MO's is nodal at the substituted sulfur and will remain



**Figure 4.** Qualitative MO diagram illustrating the effect on the frontier orbitals of  $\text{S}_3\text{N}_3^-$  (a) of the introduction of an electronegative substituent on one sulfur (b) and electron donation by the ligand into the ring  $\pi$ -system (c).



**Figure 5.** Qualitative MO diagram showing the  $\pi$ -energy levels of the  $\text{S}_3\text{N}_3^-$  ion (a), a hypothetical  $\text{S}_2\text{N}_3^-$  ion (b), and the  $\text{S}_3\text{N}_3\text{O}_2^-$  ion (c) in which some conjugation to the sulfone group (d) is assumed.

unchanged) to produce a pair of high-lying occupied  $\pi^*$  type orbitals  $a_2$  and  $b_1$ . The two visible absorptions in the visible spectrum of  $\text{S}_3\text{N}_3\text{O}^-$  can then be assigned to excitations from these two orbitals to the  $\pi^*$  LUMO  $b_1$ . A similar description of the electronic spectra of the related  $\text{Ph}_3\text{P}=\text{NS}_3\text{N}_3$  ( $\lambda_{\text{max}} = 478, 330\text{ nm}$ ) and  $\text{Ph}_3\text{As}=\text{NS}_3\text{N}_3$  ( $\lambda_{\text{max}} = 488, 336\text{ nm}$ ) derivatives (6) has recently been reported.<sup>6b</sup> For these latter molecules, the interpretation of the MCD spectra in terms of a perturbed 10- $\pi$ -electron six-atom perimeter supports the assignments.

In the case of the  $\text{S}_3\text{N}_3\text{O}_2^-$  ion, oxidation of one of the sulfur atoms to the S(VI) state produces a derivative very similar in terms of electronic structure to the recently reported  $\text{R}_2\text{PS}_2\text{N}_3$  derivatives.<sup>7,26</sup> To a first approximation one can then consider that  $\pi$ -delocalization in  $\text{S}_3\text{N}_3\text{O}_2^-$  is restricted to a five-atom N-S-N-S-N sequence containing eight  $\pi$ -electrons. The expected  $\pi$  MO ordering for such a fragment is illustrated in Figure 5. Extension of the  $\pi$ -system onto the sulfone sulfur can certainly occur, but this would more than likely require the participation of 3d orbitals on this atom, since

(32) Pearson, R. G. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2104.

(33) Salem, L. "The Molecular Orbital Theory of Conjugated Systems"; W. A. Benjamin: New York, 1966; Chapter 8.

(34) Strictly speaking, it is not valid to make a distinction between the  $\sigma$ - and  $\pi$ -systems of  $\text{S}_3\text{N}_3\text{O}^-$  and  $\text{S}_3\text{N}_3\text{O}_2^-$ , since in the solid state their structures are not planar. However, cyclic  $\pi$  type conjugation will still be present, albeit somewhat diminished relative to  $\text{S}_3\text{N}_3^-$ . In the present discussion, the terms " $\pi$ -system" and " $\pi$ -electron" are used loosely, the designation merely indicating those orbitals that interact primarily in a  $\pi$  type fashion.

the 3s and 3p orbitals will be largely involved in  $\sigma$ -bond formation. However, the extent of 3d orbital mixing into the ring  $\pi$ -system will be unlikely to affect the ordering of  $\pi$ -levels. Certainly in the case of the related  $R_2PS_2N_3$  compounds **7** ab initio Hartree-Fock-Slater calculations indicate that 3d orbitals on phosphorus stabilize the  $\pi$ -system, particularly the upper  $\pi^*$ -levels, but do not change the basic features expected for a pentadienyl-like NSNSN<sup>-</sup> species.<sup>26</sup> By analogy with the spectral assignments reported for the  $R_2PS_2N_3$  system,<sup>26</sup> we propose that the two intense visible absorption bands in  $S_3N_3O_2^-$  correspond to the  $\pi^* \rightarrow \pi^*$  excitations illustrated in Figure 5.

### Summary

The oxidation of the  $S_3N_3^-$  ion by molecular oxygen yields a complex range of products, the identification and characterization of which has been aided by <sup>15</sup>N NMR spectroscopy. The solid-state structures of the  $S_3N_3O^-$  and  $S_3N_3O_2^-$  anions (as the PPN<sup>+</sup> salts) show some structural distortions, but in solution a higher symmetry appears to be achieved (on an

NMR time scale). The origins of the intense visible absorptions exhibited by  $S_3N_3O^-$  and  $S_3N_3O_2^-$  can be understood by considering the expected perturbations on the 10- $\pi$ -electron manifold of  $S_3N_3^-$ . The transitions responsible for the observed absorptions are assigned to  $\pi^* \rightarrow \pi^*$  type excitations.

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**Registry No.** 1, 72884-86-7; 2, 81260-54-0; 3, 86176-90-1; 4, 72884-88-9; 5, 86163-11-3; PPN<sup>+</sup>N<sub>3</sub><sup>-</sup>, 38011-36-8; S<sub>4</sub>N<sub>4</sub>O<sub>2</sub>, 57932-64-6.

**Supplementary Material Available:** Tables of hydrogen atom positions, anisotropic thermal parameters for the non-hydrogen atoms, distances and angles within the two (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup> cations, and structure factor amplitudes for (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>S<sub>3</sub>N<sub>3</sub>O<sup>-</sup> and (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>S<sub>3</sub>N<sub>3</sub>O<sub>2</sub><sup>-</sup> (23 pages). Ordering information is given on any current masthead page.

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## Kinetics of the Racemization of Tris(tropolonato)silicon(IV) Perchlorate in Organic Solvents<sup>†</sup>

TOMOAKI INOUE\*

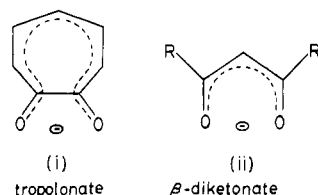
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The racemization of tris(tropolonato)silicon(IV) ion was studied in 1,1,2,2-tetrachloroethane (TCE) and acetonitrile (AN) at 30–70 °C by polarimetry. The reaction is not accompanied by detectable decomposition and ligand substitution of the complex. The following first-order rate constants (s<sup>-1</sup>), activation enthalpies (kcal/mol), and entropies (cal/(K mol)) have been obtained at 50 °C:  $2.0 \times 10^{-5}$ ,  $26.7 \pm 0.7$ ,  $1 \pm 2$  in TCE and  $2.8 \times 10^{-4}$ ,  $25.6 \pm 0.5$ ,  $4 \pm 2$  in AN. The racemization rate is promoted by trichloroacetic acid. The mechanism consistent with the activation parameters and the existence of an acid-catalyzed path is a bond rupture mechanism to give five-coordinate intermediates. An isokinetic plot together with the results of the racemization of tris( $\beta$ -diketonato)silicon(IV) also supports this mechanism.

### Introduction

A bond rupture mechanism to give five-coordinate intermediates has been proposed for intramolecular rearrangement of tris( $\beta$ -diketonato)metal complexes.<sup>1,2</sup> In contrast to this dissociative mechanism, Holm and co-workers<sup>3</sup> proposed a twisting mechanism (with no bond breaking) in the racemization of tris(tropolonato)metal complexes.

We have investigated the racemization kinetics of tris(tropolonato)silicon(IV) ([SiT<sub>3</sub>]<sup>+</sup>)<sup>4</sup> in order to determine the effects of the tropolonato chelate on the activation parameters and mechanism and to provide a comparison with the kinetic behavior of Co(III) and Al(III) tropolonato complexes. As i and ii show, tropolanate is sterically constrained to be a planar



and five-membered chelate ring in contrast to the flexible, six-membered  $\beta$ -diketonate ligand. These differences had also

led us to compare the kinetics of [SiT<sub>3</sub>]<sup>+</sup> with those of [Si( $\beta$ -dik)<sub>3</sub>]<sup>+</sup>.<sup>5</sup>

### Experimental Section

**Reagents.** Tropolone and 3-isopropyltropolone were kindly supplied by Professors Toshio Mukai and Kahei Takase in our department. We prepared tropolone following the literature procedure.<sup>6</sup> The purifications of TCE, An, pyridine, and trichloroacetic acid are described in ref 5.

**Partial Resolution.** [SiT<sub>3</sub>]<sup>+</sup> was first resolved by Ito et al.<sup>7</sup>, but the method was not given. We resolved the complex with di-benzoyl-*d*-tartaric acid as follows: The complex chloride (2 g) dissolved in water (340 mL) was cooled in an ice bath. The resolving agent (0.755 g,  $1/2$  equiv of the complex) in 0.2 M aqueous sodium hydroxide solution (26 mL) was gradually added to the complex solution. The

- (1) J. G. Gordon II and R. H. Holm, *J. Am. Chem. Soc.* **92**, 5319 (1970).
- (2) A. Y. Girgis and R. C. Fay, *J. Am. Chem. Soc.*, **92**, 7061 (1970). S. S. Minor and G. W. Everett, Jr. *Inorg. Chem.*, **15**, 1526 (1976).
- (3) (a) S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *J. Am. Chem. Soc.* **94**, 6411 (1972). (b) S. S. Eaton, G. R. Eaton, R. H. Holm, and E. L. Muetterties, *Ibid.*, **95**, 1116 (1973).
- (4) Abbreviation of ligands: T, tropolonate; 2-C<sub>3</sub>H<sub>5</sub>T, 2-isopropenyltropolonate; 2-C<sub>3</sub>H<sub>7</sub>T, 2-isopropyltropolonate; 2-RT, 2-substituted tropolonate;  $\beta$ -dik,  $\beta$ -diketonates; acac, acetylacetonate; dprm, 3,5-heptanedionate; dbm, 1,3-diphenyl-1,3-propanedionate; Me-dprm, 3-methyl-3,5-heptanedionate; Me-acac, 3-methyl-2,4-pentanedionate; tfac, 1,1,1-trifluoro-2,4-pentanedionate; hfac, 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate; triac, 3-acetyl-2,4-pentanedionate; dibm, 2,6-dimethyl-3,5-heptanedionate.
- (5) (a) T. Inoue and K. Saito, *Bull. Chem. Soc. Jpn.*, **46**, 2417 (1973); (b) T. Inoue, J. Fujita, and K. Saito, *Ibid.*, **48**, 1228 (1975).
- (6) T. Nozoe, S. Seto, H. Takeda, S. Morosawa, and K. Matsumoto, *Sci. Rep. Tohoku Univ. Ser. 1*, **36**, 126 (1952).
- (7) T. Ito, N. Tanaka, I. Hanazaki, and S. Nagakura, *Inorg. Nucl. Chem. Lett.* **5**, 781 (1969).

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<sup>†</sup> Taken in part from T. Inoue, Ph.D. Thesis, Tohoku University, 1974.