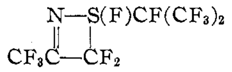
seems to be consistent with a cyclic four-membered ring compound, *viz.*



although how a compound with such a structure might result from the reaction involved is far from clear. In the final analysis attack by a perfluoroisopropyl carbanion must have been involved.

Table II lists the simple properties and the analytical data for the various compounds described in this paper.

Acknowledgments.—The authors wish to thank a colleague, Dr. Robert Hanrahan, for the use of preparative scale v.p.c. equipment and Mr. James McCully and Mr. William Blasky for their assistance in the tedious operation of the equipment for separating liquid mixtures. We are also very indebted to Dr. W. S. Brey, another colleague, and his students for obtaining the n.m.r. spectra for the various compounds involved.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ARKANSAS, FAYETTEVILLE, ARKANSAS

The Structure of Thiotrithiazyl Nitrate, $S_4N_3NO_3$

BY A. W. CORDES, R. F. KRUH, AND E. K. GORDON

Received November 30, 1964

The structure of thiotrithiazyl nitrate, $S_4N_3NO_3$, shows the $S_4N_3^+$ cation to be cyclic with six nitrogen–sulfur bonds and one sulfur–sulfur bond. The cation is planar within the experimental uncertainties. The nitrogen–sulfur distances are all nearly equal and average 1.55 Å., which suggests a bond order of about two. The sulfur–sulfur distance is 2.06 Å., a value which is a single-bond length. The SSN bond angles are 111°, the NSF angles 119°, the two equivalent SNS angles are each about 152°, and the unique SNS angle is 135°.

Sulfur nitride, S_4N_4, is the parent compound for a large number of varied products which retain from one to all eight of the original sulfur–nitrogen linkages.[1] One of the products, obtained by treating sulfur nitride with gaseous hydrogen chloride in carbon tetrachloride, is the thiotrithiazyl cation, $S_4N_3^+$. The ionic nature of this seven-atom unit is demonstrated by its ability to form a number of salts by simple metathetical reactions in aqueous solution. A structural investigation of the nitrate salt of $S_4N_3^+$ was begun in our laboratory in 1961[2] and a similar study was initiated at about the same time at Heidelberg University in the laboratory of Dr. Johannes Weiss.[3] In 1962 Weiss reported tentative parameters which indicated a cyclic structure for $S_4N_3^+$, but he was not able to ascertain whether the ring was a planar unit. Moreover, an incorrect space group was reported. The present report is an account of our determination confirming the existence of a nearly planar ring.

Experimental

The compound was prepared by dissolving S_4N_3Cl in concentrated nitric acid, and the crystals were obtained directly from this solution by allowing the hot solution to cool slowly. The yellow crystals grow in two forms: plates whose principal faces are (010) or (100), and needles elongated in the *c* direction. Goniometric study indicated holohedral monoclinic symmetry 2/m. The information used for the structural determination was obtained from both varieties. The crystals decompose upon heating or upon prolonged exposure to air.

All of the diffraction measurements were carried out at room temperature using nickel-filtered Cu Kα radiation; 1.540 Å. was used for the wave length of the radiation. The unit cell dimensions, as measured from rotation and Weissenberg photographs, are: $a = 5.84 \pm 0.02$; $b = 10.50 \pm 0.01$; $c = 12.15 \pm 0.01$ Å.; $\beta = 101 \pm 0.3°$. Systematic absences ($h0l$ for $h + l$ odd and $0k0$ for k odd) indicate the space group $P2_1/n$ (general positions: $\pm(x, y, z)$, $\pm(^1/_2 - x, ^1/_2 + y, ^1/_2 - z)$). The density was found by flotation to lie between 1.99 and 2.18 g. cm.$^{-3}$, a value which indicates four molecules per unit cell. The calculated density is 2.13 g. cm.$^{-3}$.

The data which were used to deduce the atomic positions were provided by 113 observed and 27 unobserved $0kl$ reflections and 55 observed and 14 unobserved $hk0$ reflections. Fifteen $0kl$ and eight $hk0$ reflections were not included because of evidence of secondary extinction. These reflections, of high intensity, were omitted from all of the calculations, including the final refinement. The final refinement used a total of 615 three-dimensional data.

The intensities were estimated visually with the aid of a calibrated strip. Because of the uncertainty in the intensity introduced by partial decomposition of the crystal during the measurement, no general correction was made for absorption or for shape of the reflection spot.

Determination of the Structure

Possible *y,z* coordinates were obtained from the $0kl$ data by a direct determination of phases[4] and by applying the superposition method[5] to the Patterson projection on (100). These two independent approaches agreed in general on the positions of the atoms in the

---

[1] For review articles see M. Goehring, *Quart. Rev.* (London), **10**, 437 (1956), or M. Becke-Goehring, *Progr. Inorg. Chem.*, **1**, 208 (1959).

[2] R. F. Kruh, A. W. Cordes, R. M. Lawrence, and R. G. Goforth, *Acta Cryst.*, **14**, 1306 (1961).

[3] J. Weiss, *Angew. Chem. Intern. Ed. Engl.*, **1**, 214 (1962).

[4] W. Cochran and M. M. Woolfson, *Acta Cryst.*, **8**, 1 (1955).

[5] M. J. Buerger, *ibid.*, **4**, 531 (1951).

sulfur–nitrogen cation, and it was apparent from this point on that the unit was cyclic. This approach did not, however, give any definite indication of the position of the nitrate ion. At this point in our work Dr. Weiss published his tentative atom positions. We found that we were using the same unit cell, but differed in the space group assignment. However, this difference, between $P2_1/c$ (Weiss) and $P2_1/n$ (ours), does not affect the symmetry in the *yz* projection, and we found that Weiss' ring position in this plane agreed with our own tentative assignment. We then adopted the nitrate position given by Weiss as a starting point for successive refinement with an IBM 650 computer using Fourier difference syntheses for both the *yz* and *xy* projections. The discrepancy coefficients, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, with anisotropic temperature factors for the sulfur atoms and isotropic temperature factors for the other atoms, were 0.13 for the 0*kl* data and 0.21 for the *hk*0 data at this point.

Table II

Thermal Parameters and Standard Deviations[a]

	β(1,1)	β(2,2)	β(3,3)	β(1,2)	β(1,3)	β(2.3)
S(1)	3.67 ± 0.45	0.27 ± 0.04	0.42 ± 0.03	0.09 ± 0.07	−0.12 ± 0.10	0.06 ± 0.02
S(2)	3.20 ± 0.46	0.28 ± 0.04	0.41 ± 0.03	0.09 ± 0.07	−0.07 ± 0.11	0.04 ± 0.02
S(3)	4.60 ± 0.51	0.29 ± 0.04	0.63 ± 0.04	0.14 ± 0.08	0.16 ± 0.13	0.04 ± 0.02
S(4)	3.64 ± 0.49	0.53 ± 0.04	0.47 ± 0.04	0.40 ± 0.09	−0.23 ± 0.11	−0.07 ± 0.03
N(1)	3.59 ± 1.12	0.34 ± 0.10	0.43 ± 0.09	0.13 ± 0.25	−1.01 ± 0.34	0.01 ± 0.07
N(2)	3.11 ± 0.94	0.29 ± 0.11	0.66 ± 0.11	0.43 ± 0.26	0.16 ± 0.32	0.13 ± 0.08
N(3)	2.96 ± 1.13	0.33 ± 0.12	0.60 ± 0.10	−0.37 ± 0.26	−0.24 ± 0.33	0.01 ± 0.08
N(4)	3.72 ± 1.27	0.35 ± 0.09	0.18 ± 0.07	0.24 ± 0.29	0.26 ± 0.26	0.09 ± 0.07
O(1)	5.44 ± 1.38	0.63 ± 0.10	0.63 ± 0.09	0.38 ± 0.31	0.44 ± 0.30	0.10 ± 0.09
O(2)	11.37 ± 1.87	0.56 ± 0.11	1.04 ± 0.14	1.65 ± 0.37	1.74 ± 0.40	0.34 ± 0.10
O(3)	9.59 ± 1.68	0.40 ± 0.10	0.74 ± 0.11	−0.62 ± 0.29	0.30 ± 0.36	0.02 ± 0.08

[a] All coefficients and standard deviations have been multiplied by 100.

The atomic positions and the individual anisotropic temperature factors were then adjusted by a least-squares refinement using three-dimensional data. This work was done with the Oak Ridge National Laboratory's computing facilities. The atomic scattering factors were taken from the International Tables,[6] using the values for neutral atoms. The data were weighted in a manner similar to that used by Hughes[7]: structure factors above a specified value (four times the minimum observed value) were assigned weights inversely proportional to the square of the structure factor. The temperature factor was of the form

$$[(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$$

The final positions, standard deviations, temperature factors, and bond distances and angles are shown in Tables I–III and Figure 1. Figure 2 shows the contents of the unit cell in the (100) projection and the inter-ion packing distances. Table IV compares the calculated structure factors to the experimental values. The final discrepancy factor was $R = 0.16$ for a total of 615 observed and unobserved reflections. This relatively high value of R is attributed to the intensity errors introduced by the decomposition of the crystal during the course of the measurements.

Table I

Atomic Coordinates

	x	σ (x)	y	σ (y)	z	σ (z)
S(1)	0.1839	0.0012	0.4405	0.0003	0.1193	0.0003
S(2)	0.5154	0.0013	0.3879	0.0003	0.1986	0.0003
S(3)	0.4872	0.0014	0.1113	0.0003	0.1306	0.0004
S(4)	0.0270	0.0014	0.1862	0.0004	0.0196	0.0004
N(1)	0.2357	0.0039	0.0956	0.0011	0.0564	0.0011
N(2)	0.0482	0.0040	0.3232	0.0010	0.0544	0.0013
N(3)	0.5617	0.0040	0.2439	0.0011	0.1827	0.0012
N(4)	0.0176	0.0036	0.2063	0.0011	0.3511	0.0009
O(1)	0.1034	0.0041	0.1358	0.0012	0.2781	0.0012
O(2)	0.9293	0.0049	0.1522	0.0012	0.4239	0.0014
O(3)	0.0220	0.0047	0.3234	0.0010	0.3434	0.0012

Table III

Bond Distances and Angles

Angles, deg.		Distances, Å.	
S(1)–S(2)–N(3)	111.8 ± 1.0	S(1)–S(2)	2.064 ± 0.007
S(2)–S(1)–N(2)	110.9 ± 0.8	S(2)–N(3)	1.549 ± 0.013
N(2)–S(4)–N(1)	119.0 ± 1.5	S(1)–N(2)	1.582 ± 0.016
N(3)–S(3)–N(1)	118.8 ± 1.5	S(3)–N(3)	1.550 ± 0.013
S(1)–N(2)–S(4)	153.3 ± 1.5	S(4)–N(2)	1.493 ± 0.014
S(2)–N(3)–S(3)	151.5 ± 1.3	S(4)–N(1)	1.544 ± 0.015
S(3)–N(1)–S(4)	134.4 ± 1.2	S(3)–N(1)	1.579 ± 0.018
O(1)–N(4)–O(2)	118.9 ± 2.3	S(1)–S(3)	3.863 ± 0.006
O(1)–N(4)–O(3)	119.2 ± 2.7	S(2)–S(4)	3.864 ± 0.007
O(3)–N(4)–O(2)	121.9 ± 2.8	N(4)–O(1)	1.312 ± 0.023
		N(4)–O(2)	1.238 ± 0.026
		N(4)–O(3)	1.230 ± 0.022

Discussion of the Structure

The four sulfur atoms of the $S_4N_3^-$ ring may certainly be considered coplanar. The S(2), N(1), N(2), and N(3) atoms have perpendicular distances to the plane defined by S(1), S(3), S(4) of 0.013, 0.012, 0.015, and 0.023 Å., respectively. The largest deviation from planarity in the ring, that involving N(3), amounts to a displacement of that nitrogen which is within the uncertainty of the positions in the *x* direction. The sum of the interior angles is very nearly the required 900°, being 899.7 ± 3.4°. This ring planarity is to be contrasted to the markedly puckered, or nonplanar, rings of the parent compound S_4N_4[8] and the other six- and eight-membered nitrogen–sulfur rings pre-

---

(6) J. A. Ibers in "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1962, Vol. III, p. 202.

(7) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

(8) B. D. Sharma and J. Donohue, *Acta Cryst.*, **16**, 891 (1963).

TABLE IV

OBSERVED *vs.* CALCULATED STRUCTURE FACTORS

h	k	ℓ	F obs	F calc
0	0	2	1.53	2.38
0	0	4	54.59	-53.65
0	0	6	38.81	38.67
0	0	8	15.90	14.72
0	0	10	11.51	9.18
0	0	12	25.54	-33.02
0	0	14	5.26	5.10
0	1	1	5.92	-6.68
0	1	4	16.12	-17.18
0	1	5	3.62	-5.28
0	1	6	29.27	-31.72
0	1	7	43.74	37.99
0	1	8	16.01	-11.17
0	1	9	21.27	-21.35
0	1	10	22.47	-25.08
0	1	11	4.17	-6.26
0	1	12	25.43	-28.70
0	1	13	16.33	14.69
0	1	14	13.48	14.63
0	1	15	4.61	-5.29
0	2	1	1.64	-1.10
0	2	2	16.99	-19.86
0	2	3	30.37	-45.80
0	2	4	34.42	-39.84
0	2	5	27.19	-29.87
0	2	6	37.16	-39.90
0	2	7	4.71	5.63
0	2	8	20.06	16.33
0	2	9	35.19	-40.57
0	2	10	7.13	10.35
0	2	11	9.32	11.68
0	2	12	17.76	-18.28
0	2	13	3.50	-4.38
0	2	14	2.85	-4.38
0	2	15	10.09	-14.05
0	3	1	36.07	-34.97
0	3	3	18.64	-15.95
0	3	4	18.75	16.16
0	3	5	9.21	8.61
0	3	6	45.17	43.20
0	3	7	60.52	-65.33
0	3	8	5.26	5.97
0	3	9	22.04	-16.03
0	3	10	22.69	-21.67
0	3	11	4.06	3.78
0	3	12	3.95	2.70
0	3	13	3.40	4.97
0	3	14	21.16	27.23
0	4	1	34.53	36.33
0	4	2	16.12	18.82
0	4	3	14.80	13.70
0	4	4	9.21	6.91
0	4	5	3.18	-1.98
0	4	6	15.24	12.10
0	4	7	3.62	-4.73
0	4	8	12.39	7.17
0	4	9	18.31	13.67
0	4	10	9.32	-9.03
0	4	11	28.72	34.23
0	4	12	20.50	20.28
0	4	13	7.13	8.61
0	4	14	7.78	-6.71
0	5	1	4.06	2.85
0	5	2	41.00	-41.15
0	5	3	4.28	2.36
0	5	4	14.36	6.98
0	5	5	59.31	64.24
0	5	6	30.48	23.63
0	5	7	17.32	-15.04
0	5	8	22.15	17.56
0	5	9	26.31	23.24
0	5	10	4.06	-2.63
0	5	11	24.78	26.02
0	5	12	3.51	1.31
0	5	13	9.21	-11.33
0	6	0	10.96	-9.32
0	6	1	17.54	20.48
0	6	2	40.02	36.23
0	6	3	47.80	45.75
0	6	4	49.99	38.13
0	6	5	23.46	-17.25
0	6	6	3.95	6.14
0	6	7	57.23	-48.83
0	6	8	4.17	-5.01
0	6	9	26.31	21.00
0	6	10	12.72	-12.52
0	6	11	3.73	-4.38
0	6	12	17.54	17.86
0	6	13	11.07	-12.37
0	7	1	3.51	.71
0	7	2	51.31	45.94
0	7	3	33.22	-25.60
0	7	4	54.38	-51.91
0	7	5	45.17	-32.69
0	7	6	4.06	-1.01
0	7	7	41.55	29.89
0	7	8	5.92	-7.85
0	7	9	5.70	8.07
0	7	10	18.86	-16.67
0	7	11	10.52	-11.54
0	7	12	6.14	-7.93
0	8	0	13.48	-10.59
0	8	1	5.48	7.03
0	8	2	55.80	-52.67
0	8	3	35.85	28.35
0	8	4	4.06	1.94
0	8	5	26.20	-22.12
0	8	6	4.17	-4.53
0	8	7	11.62	-7.77
0	8	8	28.28	-26.70
0	8	9	23.80	24.00
0	8	10	9.65	9.04
0	8	11	10.96	-10.05
0	9	1	26.09	26.00
0	9	2	4.06	6.23
0	9	3	9.32	-6.65
0	9	4	29.49	29.64
0	9	5	65.56	-56.64
0	9	6	18.20	14.83
0	9	7	24.78	19.31
0	9	8	3.62	-4.37
0	9	9	9.32	9.07
0	9	10	12.61	15.17
0	9	11	13.05	-16.24
0	10	0	26.20	23.21
0	10	1	18.53	-16.99
0	10	2	4.06	2.44
0	10	3	20.39	-21.34
0	10	4	11.40	12.84
0	10	5	27.63	24.07
0	10	6	23.57	19.04
0	10	7	24.56	25.09
0	10	8	3.18	-3.97
0	10	9	13.27	-13.26
0	11	1	29.93	27.67
0	11	2	12.06	-11.23
0	11	3	3.73	-1.85
0	11	4	16.01	12.30
0	11	5	3.40	-2.75
0	11	6	14.03	-16.67
0	11	7	12.50	14.14
0	12	0	14.69	-13.10
0	12	1	3.29	-2.60
0	12	2	14.36	14.76
0	12	3	35.41	-32.82
0	12	4	11.18	10.08
0	12	5	11.73	11.54
0	13	1	12.72	-15.50
0	13	2	2.19	-1.96
0	13	3	6.25	-9.39
1	0	5	19.77	-20.57
1	0	-5	20.73	-15.57
1	0	7	34.72	31.71
1	0	-7	5.86	-2.03
1	0	9	11.81	-12.14
1	0	-9	31.67	28 11
1	0	11	8.57	-6.83
1	0	-11	17.32	20.73
1	1	0	11.57	14.02
1	1	1	19.42	-39.20
1	1	-1	23.36	-36.69
1	1	2	5.34	5.31
1	1	-2	40.85	-45.87
1	1	-3	25.02	31.43
1	1	4	56.07	57.08
1	1	5	18.28	-13.82
1	1	6	25.89	-24.85
1	1	-6	37.62	33.85
1	1	7	20.30	-17.18
1	1	-7	9.36	9.92
1	1	8	42.87	-43.87
1	1	-8	25.37	-24.79
1	1	9	33.42	-34.71
1	1	-9	25.19	29.88
1	1	10	34.64	37.58
1	1	-10	3.76	2.68
1	1	11	12.07	10.06
1	1	-11	7.79	-6.79
1	1	12	11.28	9.86
1	2	0	1.57	-1.79
1	2	1	23.88	-34.75
1	2	-1	15.83	18.20
1	2	2	37.97	50.52
1	2	-2	24.49	-42.07
1	2	-3	27.56	-48.16
1	2	4	2.45	-3.36
1	2	5	8.57	-6.21
1	2	-5	24.76	-32.49
1	2	6	42.25	-63.81
1	2	-6	39.10	55.23
1	2	7	20.73	16.87
1	2	-7	13.65	-10.51
1	2	8	11.28	10.52
1	2	-8	31.41	22.06
1	2	9	16.88	-12.99
1	2	-9	8.84	-9.41
1	2	10	17.32	15.93
1	2	-10	3.85	-5.72
1	2	11	12.07	-10.40
1	2	-11	3.85	5.68
1	2	12	31.49	-29.64
1	2	-12	29.13	25.10
1	3	2	6.39	-8.81
1	3	2	13.73	11.89
1	3	-2	25.11	-35.95
1	3	3	25.98	26.64
1	3	-3	9.89	10.66
1	3	4	28.52	-35.27
1	3	5	12.77	12.61
1	3	-5	46.10	53.07
1	3	6	27.99	-23.52
1	3	-6	11.28	7.48
1	3	7	10.76	8.96
1	3	-7	28.61	-27.17
1	3	8	3.67	2.66
1	3	-8	3.50	-1.17
1	3	9	3.85	2.96
1	3	-9	16.53	-16.00
1	3	10	24.49	-14.21
1	3	-10	29.83	-27.11
1	3	11	23.71	20.59
1	3	12	10.85	7.05
1	4	0	22.92	23.16
1	4	1	40.77	50.24
1	4	-1	23.01	25.70
1	4	2	11.02	7.10
1	4	-2	18.37	-16.58
1	4	3	45.66	-49.13
1	4	-3	35.43	-45.41
1	4	4	18.02	-15.15
1	4	-4	26.86	-28.94
1	4	5	27.47	20.28
1	4	-5	2.89	-2.69
1	4	6	25.72	-18.34
1	4	-6	31.32	24.00
1	4	7	3.59	-1.66
1	4	-7	21.35	-15.18
1	4	8	41.12	48.77
1	4	-8	14.00	8.45
1	4	9	30.01	21.27
1	4	-9	23.97	18.86
1	4	10	38.49	38.77
1	4	-10	21.26	-16.86
1	4	11	11.55	-8.56
1	4	-11	3.85	-5.62
1	4	12	10.32	7.08
1	4	-12	25.28	-26.64
1	5	0	23.62	19.10
1	5	1	2.71	-3.64
1	5	-1	23.71	-20.43
1	5	2	48.38	56.91
1	5	-2	33.24	47.45
1	5	3	29.31	23.85
1	5	-3	25.28	20.10
1	5	4	22.05	-13.86
1	5	-4	29.74	-32.29
1	5	5	40.59	43.40
1	5	-5	14.08	-14.84
1	5	6	31.49	27.13
1	5	-6	3.32	4.41
1	5	7	23.44	13.27
1	5	-7	31.93	-28.09
1	5	8	42.08	53.86
1	5	-8	45.84	48.77
1	5	9	24.49	-18.72
1	5	-9	14.96	-16.86
1	5	10	29.13	-22.58
1	5	-10	8.66	-8.09
1	5	-11	16.62	18.26
1	6	0	30.01	35.19
1	6	1	31.93	32.68
1	6	-1	18.98	18.00
1	6	2	9.89	-8.39
1	6	-2	13.65	-6.87
1	6	3	32.46	31.70
1	6	-3	24.41	-17.32
1	6	4	41.55	-41.49
1	6	-4	14.70	9.91
1	6	5	27.56	25.47
1	6	-5	34.29	32.72
1	6	6	16.62	12.29
1	6	-6	27.82	-20.51
1	6	7	17.15	-12.35
1	6	-7	29.04	17.72
1	6	8	3.85	-3.96
1	6	-8	32.19	22.63
1	6	9	12.07	8.06
1	6	-9	3.85	2.77
1	6	-10	23.88	19.43
1	6	-11	3.50	-2.60
1	6	-12	13.91	-14.83
1	7	0	10.59	10.07
1	7	-1	67.10	64.57
1	7	2	34.47	-34.63
1	7	-2	10.76	9.42
1	7	3	22.39	-16.35
1	7	-3	34.64	34.50
1	7	4	8.14	-5.19
1	7	-4	3.59	3.12
1	7	5	23.79	14.02
1	7	-5	23.27	-17.91
1	7	6	12.16	6.36
1	7	-6	37.88	-39.48
1	7	7	34.73	-33.22
1	7	-7	21.17	21.19
1	7	8	3.85	-4.07
1	7	-8	12.25	-12.69
1	7	9	19.95	-20.43
1	7	-9	3.77	.75
1	7	10	3.32	.82
1	7	-10	19.60	19.05
1	7	11	22.05	-23.57
1	7	-11	17.67	21.09
1	8	0	16.36	13.58
1	8	1	28.52	-32.87
1	8	-1	73.13	-70.65
1	8	2	3.76	1.03
1	8	-2	16.45	16.04
1	8	3	33.77	34.36
1	8	-3	8.31	-9.31
1	8	4	8.57	-6.87
1	8	-4	11.98	-9.65
1	8	5	34.64	-32.76
1	8	-5	8.57	-8.87
1	8	6	30.01	24.13
1	8	-6	34.64	-35.90
1	8	7	11.98	-10.59
1	8	-7	12.16	8.17
1	8	8	16.18	-20.35
1	8	-8	16.80	16.68
1	8	9	14.87	-15.00
1	8	-9	22.48	-25.57
1	8	10	13.03	-13.39
1	9	0	12.16	11.40
1	9	1	24.41	21.64
1	9	-1	3.85	-2.98
1	9	2	38.67	-49.73
1	9	-2	3.85	-1.11
1	9	3	12.25	10.36
1	9	-3	12.25	-11.35
1	9	4	3.85	1.28
1	9	-4	12.25	12.31
1	9	5	3.85	-1.12
1	9	-5	8.66	7.70
1	9	6	16.62	15.70
1	9	-6	11.98	-12.22
1	9	7	15.75	16.36
1	9	-7	16.44	-22.27
1	9	8	14.52	-14.47
1	9	-8	21.96	-25.80
1	9	9	12.77	13.52
1	9	-9	9.97	-9.00
1	9	-10	17.41	20.60
1	10	0	17.23	-11.18
1	10	1	3.85	2.26
1	10	-1	3.85	-13.13
1	10	2	12.07	12.40
1	10	-2	3.85	-3.20
1	10	3	33.68	39.92
1	10	-3	34.03	35.57
1	10	4	11.63	13.17
1	10	5	3.59	-.78
1	10	-5	16.36	19.11
1	10	6	10.59	-9.59
1	10	-6	15.66	19.11
1	10	7	19.42	-18.30
1	10	-7	10.41	5.73
1	10	8	12.07	11.02
1	11	0	3.59	4.17
1	11	1	31.67	41.36
1	11	-1	15.92	-19.70
1	11	2	3.50	-3.86
1	11	-2	22.39	24.15
1	11	3	3.41	1.98
1	11	-3	15.48	-16.96
1	11	4	10.24	10.63
1	11	-4	10.59	11.22
1	11	5	19.25	-19.39
1	11	6	12.33	12.09
1	12	0	24.51	-22.46
1	13	0	8.47	-8.08
2	0	-2	33.25	26.53
2	0	4	3.77	-9.26
2	0	-4	38.77	35.69
2	0	6	49.67	54.50
2	0	-6	48.60	53.07
2	0	8	5.52	-6.27
2	0	-8	4.98	-6.28
2	0	10	5.79	4.17
2	0	-10	5.65	4.38
2	0	-12	5.65	7.98
2	1	1	27.19	41.15
2	1	-1	1.75	1.66
2	1	2	2.83	-5.01
2	1	-2	21.00	27.02
2	1	3	19.92	21.99
2	1	-3	51.83	-48.34
2	1	4	3.77	-.65
2	1	-4	23.83	-19.76
2	1	5	47.25	-54.86
2	1	-5	25.17	-20.93
2	1	6	38.50	-42.77
2	1	-6	18.04	20.35
2	1	7	32.98	35.44
2	1	8	5.52	-6.29
2	1	-8	4.98	2.87
2	1	9	20.06	23.84
2	1	-9	22.75	20.06
2	1	10	15.21	-19.30
2	1	-10	17.90	13.40
2	1	-11	18.31	-19.51
2	1	-12	30.96	26.45
2	2	1	2.83	5.26
2	2	-1	11.04	11.69
2	2	2	31.77	-40.36
2	2	-2	16.69	-17.88
2	2	-3	13.19	14.83
2	2	4	4.04	6.09
2	2	-4	3.37	4.59
2	2	5	15.48	20.65
2	2	-5	26.65	-24.54
2	2	6	4.85	3.80
2	2	-6	46.04	-42.19
2	2	7	23.69	27.42
2	2	-7	46.44	-37.78
2	2	8	5.65	-2.98
2	2	-8	16.02	-15.23
2	2	9	28.94	-33.13
2	2	-9	66.77	60.64
2	2	-10	12.79	15.37
2	2	-11	5.79	-3.93
2	2	-12	5.65	-2.11
2	3	0	10.90	-13.92
2	3	1	3.37	1.56
2	3	-1	16.96	-17.23
2	3	2	11.31	-8.29
2	3	-2	22.62	23.32
2	3	3	32.85	-33.61
2	3	-3	7.67	-9.07
2	3	4	54.38	51.45
2	3	-4	42.40	-39.92
2	3	5	12.38	-10.58
2	3	-5	9.15	-7.93
2	3	6	16.15	18.38
2	3	-6	4.44	4.27
2	3	7	38.50	-37.35
2	3	-7	46.17	-33.12
2	3	8	5.65	-4.45
2	3	-8	13.87	-13.27
2	3	9	5.79	2.81
2	3	-9	24.90	-19.55
2	3	-10	5.79	-6.85
2	3	-11	5.79	-11.03
2	4	0	39.30	-53.90
2	4	1	17.90	20.06
2	4	-1	42.40	33.54
2	4	2	24.50	24.84
2	4	-2	30.02	27.02
2	4	3	27.33	-23.47
2	4	-3	3.90	1.10
2	4	4	32.85	31.51
2	4	-4	4.17	-2.93
2	4	5	19.38	21.49
2	4	-5	51.69	-42.27
2	4	6	5.38	-3.85
2	4	-6	4.85	-6.06
2	4	7	50.21	51.71
2	4	-7	19.92	-17.09
2	4	8	5.79	-3.17
2	4	-8	5.52	-5.59
2	4	9	18.17	17.19
2	4	-9	22.08	16.19
2	4	-10	5.65	-4.60
2	4	-11	5.65	-1.63
2	5	0	13.32	-13.62
2	5	1	4.30	1.04
2	5	-1	21.00	17.65
2	5	2	27.46	25.02
2	5	-2	31.63	-30.18
2	5	3	21.27	16.70
2	5	-3	32.71	30.94
2	5	4	50.21	40.69
2	5	-4	32.58	28.86
2	5	5	60.58	65.44
2	5	-5	57.48	49.54
2	5	6	5.52	-5.30
2	5	-6	19.92	13.84
2	5	7	23.69	-24.18
2	5	-7	29.75	-27.02
2	5	8	5.79	-8.30
2	5	-8	12.65	-10.59
2	5	9	5.65	-2.88
2	5	-9	5.79	4.92
2	5	-10	22.35	-23.62
2	5	-11	27.46	29.00
2	6	0	24.77	25.69
2	6	1	12.79	-12.76
2	6	-1	25.98	28.11
2	6	2	49.94	52.74
2	6	-2	33.92	32.46
2	6	3	5.12	5.02
2	6	-3	4.85	-5.78
2	6	4	5.38	-8.30
2	6	-4	32.04	25.76
2	6	5	30.69	-32.10
2	6	-5	23.56	-19.25
2	6	6	18.17	-12.63
2	6	-6	7.81	4.38
2	6	7	18.31	-12.78
2	6	-7	31.10	27.09
2	6	8	5.65	-3.00
2	6	-8	18.31	12.17
2	6	9	5.38	10.17
2	7	0	13.87	-14.22
2	7	1	25.04	-23.33
2	7	-1	5.25	-1.52
2	7	2	38.37	28.93
2	7	-2	68.92	-66.57
2	7	3	5.52	-3.00
2	7	-3	5.38	-2.21
2	7	4	45.77	-41.56
2	7	-4	69.33	56.79
2	7	5	5.79	3.51
2	7	-5	12.52	-7.59
2	7	6	25.98	-26.12
2	7	-6	31.37	22.71
2	7	7	18.04	13.34
2	7	8	24.23	-29.94
2	7	9	22.21	-22.28
2	8	0	21.81	21.92
2	8	1	5.65	-4.77
2	8	-1	5.65	-2.97
2	8	2	25.58	-25.08
2	8	-2	61.92	-51.49
2	8	3	5.79	6.27
2	8	-3	12.79	-11.17
2	8	4	23.96	-22.27
2	8	-4	54.52	-43.22
2	8	5	22.35	-19.62
2	8	-5	28.94	23.51
2	8	6	17.77	-17.21
2	8	-6	5.79	3.49
2	8	7	16.96	-14.25
2	8	8	4.98	.87
2	8	9	16.83	13.67
2	9	0	5.79	5.87
2	9	1	20.06	-19.03
2	9	-1	5.79	-.43
2	9	2	5.79	4.90
2	9	-2	22.48	23.60
2	9	3	5.79	-1.87
2	9	-3	22.48	25.23
2	9	4	5.65	8.44
2	9	-4	15.21	-19.13
2	9	5	21.13	-16.50
2	9	-5	31.23	-28.82
2	9	6	5.25	8.05
2	9	-6	5.52	-12.18
2	9	7	18.58	20.81
2	10	0	35.54	42.75
2	10	1	5.52	.14
2	10	-1	5.65	-2.99
2	10	-2	21.67	-22.54
2	10	-3	14.67	10.18
2	10	-4	21.13	-16.29
2	10	-5	5.25	1.67
2	10	-6	22.62	29.17
2	11	0	13.74	11.56
2	11	-2	35.40	33.85
2	11	-3	15.48	15.82
2	11	-4	21.27	-19.34
2	12	0	12.71	-10.10
3	1	0	36.53	28.69
3	2	0	19.47	-17.22
3	3	0	2.29	-3.67
3	4	0	5.38	-5.23
3	5	0	16.38	14.63
3	6	0	3.89	2.69
3	7	0	35.27	-29.73
3	8	0	2.98	.32
3	9	0	15.46	-14.03
3	10	0	3.66	-3.51
3	11	0	2.18	-2.42
3	12	0	1.49	-3.43
4	1	0	29.43	-21.86
4	2	0	16.60	-12.02
4	3	0	36.30	28.84
4	4	0	37.45	-27.95
4	5	0	31.49	23.22
4	6	0	9.16	-7.76
4	7	0	2.86	-.52
4	8	0	8.70	4.23
4	9	0	2.52	-.49
4	10	0	28.17	31.75
4	11	0	6.53	-8.35
5	1	0	9.16	-6.80
5	2	0	26.00	-23.63
5	3	0	13.05	-13.37
5	4	0	9.16	-7.65
5	5	0	12.71	11.83
5	6	0	2.75	2.45
5	7	0	2.52	-1.99
5	8	0	7.10	8.91
5	9	0	9.85	11.39
6	0	0	22.79	23.89
6	1	0	14.89	-16.25
6	2	0	2.63	3.52
6	3	0	2.63	-1.31
6	4	0	9.50	-9.62
6	5	0	2.29	-1.09
6	6	0	2.86	-6.50
6	7	0	2.63	-6.96
7	1	0	8.13	2.87
7	2	0	1.72	-4.28
7	3	0	8.47	-3.23
7	4	0	5.38	7.48

pared from S_4N_4, *i.e.*, $S_4N_4H_4$,[9] $S_4N_4F_4$,[10] $S_3N_3Cl_3$,[11] and $S_3N_3O_3Cl_3$.[12] The sulfur–nitrogen bonds have an average length of 1.55 Å. in the $S_4N_3^+$ ring, a value which is shorter than that in S_4N_4 (1.63 Å.) and which has been found previously only in one of the two S–N bond lengths found in $S_4N_4F_4$. On the basis of a correlation chart of bond length *vs.* bond order proposed for sulfur–nitrogen bonds,[13] this bond has an order of

---

[9] R. L. Sass and J. Donohue, *Acta Cryst.*, **11**, 497 (1958).

[10] G. A. Wiegers and A. Vos, *ibid.*, **14**, 562 (1961).

[11] G. A. Wiegers and A. Vos, *Proc. Chem. Soc.*, 387 (1962).

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

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

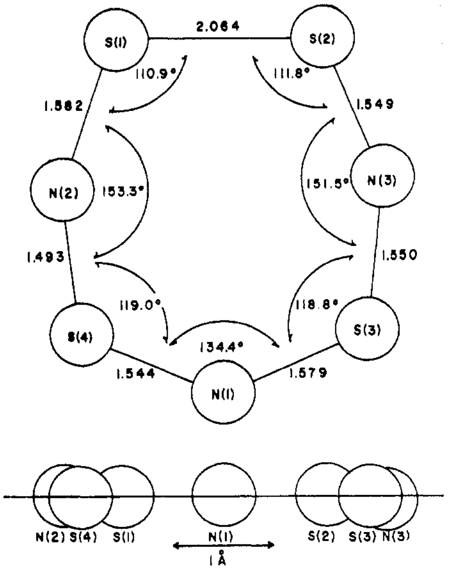


Figure 1.—The view of the $S_4N_3{}^+$ cation ring perpendicular and parallel to the plane of the ring.

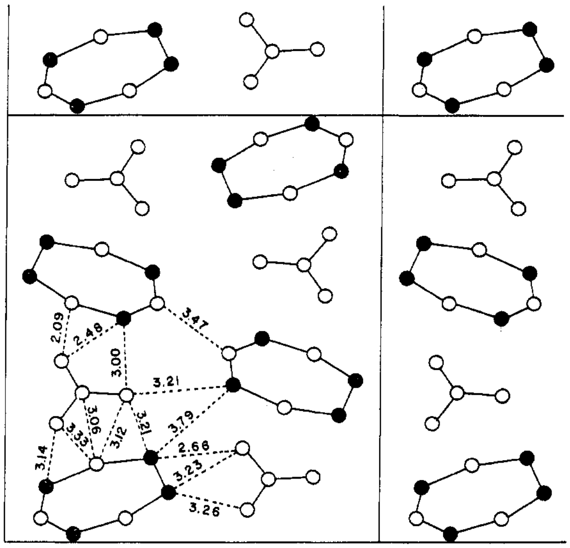


Figure 2.—Projection of $S_4N_3NO_3$ on (100).

approximately 2.1. On the other hand, the sulfur–sulfur distance of 2.06 Å. is equal to, if not slightly greater than, that found in elemental sulfur and a large number of sulfur compounds which are assumed to have singly bonded sulfurs.[14] Qualitatively, the bond distances indicate that the multiple bonding in the unit, whether it is thought to originate by either dπ–pπ overlap or by delocalization of electrons in the ring, results in a considerable increase of electron density between the N–S linkages but not between the sulfur atoms.

The thermal anisotropy indicated by the temperature factors shows a large amount of atomic motion parallel to the x axis for both the cation and the nitrate ion. Since the plane of the nitrate ring is almost exactly perpendicular to this axis, and the plane of the cation ring is nearly so also, the anisotropy is such that thermal motion out of the plane of the ions is greater than the motion within the plane, a common characteristic of ring systems. It is also likely that the large $\beta(1,1)$ temperature factor and the large uncertainties in both the $\beta(1,1)$ factors and the x coordinates in general are a result of the lack of reflections with higher values of h; most of the observed data were $0kl$, $1kl$, or $2kl$ reflections.

The distances between ring units show no serious packing problems. Several of the nitrate–ring distances are shorter than the sum of the van der Waals radii for the atoms involved, as shown in Figure 1. It appears that the nitrate ion is crowded into a pocket formed by six cation rings.

The thermal anisotropy and the bond length for O(1) in the nitrate ring is worthy of note inasmuch as these resemble the characteristics of the unique oxygen in nitric acid and thus suggest the presence of a hydrogen atom in the molecule. The unique nitrogen–oxygen bond distance in nitric acid is 1.30 Å.,[15] a value identical, within standard deviations, with that found for the N(4)–O(1) bond here. The bond angles, on the other hand, do not parallel the nitric acid structure: in nitric acid they are 134, 113, and 113°. The thermal anisotropy is probably caused by the packing considerations mentioned above. We have, moreover, found no evidence for the presence of hydrogen on the ring from the infrared analysis of the chloride salt or by direct analysis of the chloride using the Zerewitinoff–Tschugaeff method, and thus we are reluctant to suggest the presence of a hydrogen atom solely on the basis of the distortion of the nitrate ion. A trial structure which included a hydrogen atom at coordinates 0.147, 0.123, and 0.204 did not change the discrepancy factor.

A large portion of this work was done as an undergraduate research project.

Acknowledgments.—We are indebted to the National Science Foundation's Undergraduate Research Participation Program for supporting this work and to the University of Arkansas Research Committee for computing grants. We especially wish to thank Dr. John H. Burns of the Oak Ridge crystallography group for help in the least-square refinements.

---

(14) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

(15) V. Luzzati, *Acta Cryst.*, **4**, 120 (1951).