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THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRATHIAZYL TETRA-BIS-(TRIFLUOROMETHYL) NITROXIDE

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SUMMARY

The crystal structure of $[NSON(CF_3)_2]_4$ has been determined by single crystal X-ray diffraction. The crystals are tetragonal, $I\bar{4}$, $a = b = 16.73(1)$, $c = 4.73(1)$ Å, $Z = 2$. The molecule possesses an eight-membered N_4S_4 ring with a crystallographic inverse tetrad axis at its centre; the nitroxyl radicals are attached to the sulphur atoms. The two independent S–N bond lengths are 1.56(1) and 1.62(1) Å; the geometry of the $N_4S_4O_4$ moiety is similar to that of $N_4S_4F_4$.

INTRODUCTION

An X-ray crystallographic study of $[NSON(CF_3)_2]_4$ has been undertaken in order to provide some structural insight into the chemistry of the thiazyl nitroxides as reported in the preceding paper[1]. In particular, such a study was necessary to establish the nature of the $[NS]_4$ ring, and to discover whether there was any stereochemical basis for the chemical inertness of this compound.

A conventional σ-bonding scheme has been found adequate to account for the crown structure[2] of $S_4N_4H_4$, but the S–N–S angles of 122° imply some delocalisation of the nitrogen lone pairs into the vacant sulphur 3d orbitals. The unusual D_{2d} cage structure[3] of S_4N_4 itself, on the other hand, implies some electron delocalisation over the whole molecule. Finally, in $N_4S_4F_4$, the π-bonds must be at least partly localised, since the two independent S–N bond lengths are significantly different[4].

In view of the stability of the $ON(CF_3)_2$ free radical, it was not obvious whether one or none of these three structural models would be appropriate in this case.

EXPERIMENTAL

Needle-shaped crystals, suitable for single crystal X-ray diffraction, were obtained[1] directly from the reaction of N_4S_4 with liquid $ON(CF_3)_2$, and were sealed into Lindemann glass-capillary tubes. Intensities were determined visually from equi-inclination Weissenberg photographs taken with a crystal mounted about the Z (needle) axis and using Ni-filtered Cu-$K\alpha$ radiation (layers $hk0$ to $hk3$ inclusive). Lorentz, polarisation and absorption corrections were applied, the latter being calculated exactly for a cylinder with $\mu r = 0.38$, where μ is the linear absorption coefficient and r the radius of the cylinder. Unit-cell dimensions were obtained from powder photographs, taken with a Guinier focussing camera and using silicon as an internal calibrant ($a = 5.4306$ Å), and indexed using the approximate unit-cell constants and intensity data from the Weissenberg photographs. The estimated standard deviations in the unit-cell dimensions were multiplied by a factor of two to allow for possible systematic errors.

Crystal data

$C_8F_{24}N_8O_4S_4$, mol. wt. 856.4, tetragonal, Laue group $4/m$, $a = b = 16.73\ (1)$, $c = 4.73(1)$ Å, $U = 1323$ Å^3, $d_c = 2.15$ for $Z = 2$ (consistent with approximate density determination by flotation). Systematic absences: hkl, $h+k+l \neq 2n$. The space group is thus $I\bar{4}$ or $I4$.

Structure solution and refinement

For either of the two possible space groups, the [001] projection of the unit-cell is halved, and has the plane group $p4$. This projection was solved by a novel least-squares multi-solution application of Sayre's equation[5]; of the six sign-combinations investigated, one was clearly more internally consistent than the others. An E-map calculated from this combination gave essentially the correct structure, with the exception of a few spurious peaks and some difficulties arising from overlapping atoms in the CF_3 groups. Using the information from the projection, the three-dimensional structure was solved by trial and error; the only solution to refine successfully was in the space group $I\bar{4}$. All the atoms lie in general positions of the type $(x, y, z; -x, -y, z; y, -x, -z; -y, x, z) + (0,0,0; \frac{1}{2},\frac{1}{2},\frac{1}{2})$.

The structure was refined by a full-matrix least-squares procedure, with the initial use of isotropic temperature factors for all the atoms; the weighting scheme adopted on the basis of an analysis of variance was: $\omega = 1/(1 + |F_0| + 0.0003\ F_0{}^2)$. In the final stage of the refinement a total of 88 parameters was varied simultaneously, including three interlayer scale factors, anisotropic temperature factors for the sulphur and fluorine atoms only, and the Zachariasen secondary extinction coefficient[6]. The introduction of anisotropic temperature factors for the fluorine atoms was found to be highly significant. Complex neutral-atom scattering

TABLE 1

OBSERVED AND CALCULATED STRUCTURE FACTORS*

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h	k	l	$\vert F_o\vert$	$\vert F_c\vert$	ϕ
2	0	0	5.2	2.9	141.8
4	0	0	46.2	44.6	0.3
6	0	0	97.5	106.1	1.1
8	0	0	15.4	8.5	165.7
10	0	0	19.7	23.4	5.8
12	0	0	14.9	14.5	1.1
14	0	0	9.4	8.4	181.8
16	0	0	41.2	43.9	2.1
18	0	0	12.1	9.9	6.3
19	1	0	6.7	6.1	3.7
17	1	0	17.8	16.9	3.2
15	1	0	8.3	7.9	359.7
11	1	0	30.5	30.1	2.0
-9	1	0	34.6	39.5	3.5
-7	1	0	42.7	42.2	2.1
-5	1	0	89.6	94.4	180.8
-3	1	0	111.0	104.0	0.5
-1	1	0	39.7	33.6	4.3
3	1	0	25.8	20.3	178.4
5	1	0	13.7	14.0	0.7
7	1	0	33.3	27.6	176.6
9	1	0	17.7	21.6	7.4
11	1	0	26.4	26.3	3.6
13	1	0	10.2	8.3	359.4
15	1	0	8.2	6.4	176.9
17	1	0	18.9	19.2	4.4
19	1	0	4.7	3.4	11.4
14	2	0	17.7	17.3	189.6
12	2	0	19.5	17.9	183.9
10	2	0	30.0	30.5	2.0
-8	2	0	19.9	18.0	4.9
-6	2	0	73.3	72.4	181.3
-4	2	0	55.4	59.3	182.0
-2	2	0	48.2	45.6	179.7
4	2	0	61.6	68.9	181.5
6	2	0	21.5	20.7	180.6
8	2	0	41.2	43.3	3.5
10	2	0	19.2	20.3	3.9
14	2	0	13.4	11.5	181.6
16	2	0	9.5	9.2	4.7
18	2	0	10.4	9.3	5.6
15	3	0	5.9	6.2	189.3
13	3	0	26.4	28.6	184.4
-9	3	0	38.3	39.4	180.4
-7	3	0	15.8	18.1	183.4
-5	3	0	22.1	19.0	187.4
-3	3	0	30.2	25.4	357.0
5	3	0	66.7	74.6	182.1
7	3	0	55.8	59.7	180.8
9	3	0	56.7	60.5	1.5
1	3	0	20.2	26.8	181.4
3	3	0	10.3	9.0	187.4
5	3	0	4.8	3.6	183.0
7	3	0	22.6	23.1	2.6
9	3	0	6.5	6.6	3.0
10	4	0	6.7	6.3	184.0
4	4	0	19.6	15.0	185.7
2	4	0	36.0	39.0	183.1
0	4	0	4.0	4.6	184.3
8	4	0	34.3	32.1	181.1
-6	4	0	81.9	84.6	182.4
-4	4	0	136.9	138.2	181.5
6	4	0	78.5	80.7	359.6
8	4	0	21.6	21.4	179.9
0	4	0	13.8	11.2	182.5
2	4	0	30.3	30.1	183.3
4	4	0	15.1	14.5	185.3
5	5	0	11.7	12.8	183.9
3	5	0	39.5	40.1	182.7
1	5	0	9.7	10.7	182.1
9	5	0	3.9	2.7	4.2
-7	5	0	27.7	30.1	182.2
-5	5	0	49.6	51.0	183.4
7	5	0	10.2	7.7	186.0
9	5	0	29.7	26.7	1.3
1	5	0	13.0	12.6	186.2
3	5	0	23.9	25.4	184.5
5	5	0	25.3	24.8	182.8
8	6	0	6.7	8.4	5.0
4	6	0	40.9	40.1	182.0
0	6	0	50.2	50.8	1.7
8	6	0	14.2	13.0	3.5
6	6	0	66.4	65.4	359.8
8	6	0	33.7	33.9	180.7
0	6	0	21.1	21.8	359.0
4	6	0	32.5	35.9	182.7
9	7	0	10.3	11.2	3.0
7	7	0	7.2	5.1	9.1
5	7	0	16.9	15.0	2.0
1	7	0	22.3	22.3	2.7
9	7	0	40.8	36.7	3.1
7	7	0	22.6	20.9	2.1
9	7	0	36.1	34.4	2.5
1	7	0	13.6	12.9	182.0
3	7	0	43.0	45.5	182.3
5	7	0	9.9	10.7	181.6
8	8	0	13.9	14.0	4.5
2	8	0	4.7	6.2	5.8
0	8	0	26.2	22.1	5.3
6	8	0	54.9	58.4	2.7
0	8	0	23.4	22.9	179.2
2	8	0	8.2	7.9	182.6
4	8	0	3.4	1.5	184.4
8	8	0	6.0	7.2	5.2
9	9	0	5.5	6.1	4.9
5	9	0	8.9	5.6	2.8
3	9	0	27.8	27.9	181.2
1	9	0	16.4	12.8	5.5
9	9	0	50.1	53.9	2.5
1	9	0	25.0	25.3	2.2
3	9	0	17.2	14.9	6.5

h	k	l	$\vert F_o\vert$	$\vert F_c\vert$	ϕ
15	9	0	10.5	10.5	4.1
17	9	0	14.0	12.6	4.6
19	9	0	7.4	7.7	3.7
-18	10	0	7.0	6.8	3.8
-14	10	0	16.4	15.8	182.7
-12	10	0	8.3	7.1	181.5
-10	10	0	29.5	30.2	2.5
12	10	0	10.7	7.6	1.8
16	10	0	10.4	9.1	5.7
18	10	0	9.0	9.9	4.7
-15	11	0	10.7	9.3	184.0
-13	11	0	9.2	7.0	186.8
-11	11	0	6.8	5.3	181.0
13	11	0	22.5	19.5	182.3
15	11	0	8.1	6.9	3.8
17	11	0	8.8	7.6	5.3
-14	12	0	15.9	13.8	185.0
-15	13	0	5.9	4.4	188.6
-13	13	0	16.6	13.9	184.8
-14	14	0	6.8	6.7	184.8
-8	-19	1	6.2	8.2	4.0
0	-19	1	6.9	6.9	8.2
2	-19	1	7.8	7.9	51.3
4	-19	1	6.4	7.9	82.1
8	-19	1	4.8	5.7	10.0
-7	-18	1	11.9	13.8	15.5
-1	-18	1	9.4	10.6	46.7
3	-18	1	8.7	10.6	19.2
9	-18	1	7.2	9.8	5.7
0	-17	1	20.5	23.9	1.7
2	-17	1	10.2	11.7	9.0
4	-17	1	8.1	9.1	59.4
10	-17	1	7.0	6.9	358.4
-11	-16	1	2.6	3.9	175.8
-7	-16	1	10.5	12.1	307.1
-3	-16	1	5.0	5.3	102.7
-1	-16	1	15.9	18.3	357.1
1	-16	1	21.4	23.4	349.6
3	-16	1	12.3	12.9	50.1
5	-16	1	6.9	6.1	118.9
11	-16	1	5.2	5.7	10.0
-12	-15	1	7.2	7.3	159.4
-10	-15	1	6.3	6.4	246.7
-8	-15	1	11.8	13.3	331.4
-2	-15	1	9.6	9.3	244.4
0	-15	1	5.1	8.1	279.6
2	-15	1	12.0	12.0	222.6
4	-15	1	12.5	12.2	164.5
6	-15	1	14.2	14.8	187.7
-13	-14	1	8.3	9.1	179.4
-11	-14	1	11.1	11.7	203.2
-9	-14	1	12.1	13.2	235.2
-5	-14	1	24.0	24.4	189.6
-3	-14	1	23.4	23.9	162.5
-1	-14	1	10.2	6.6	195.1
1	-14	1	8.8	8.4	257.9
3	-14	1	8.8	8.7	212.4
5	-14	1	19.8	21.6	175.6
7	-14	1	19.0	18.8	189.5
9	-14	1	11.0	10.9	339.1
13	-14	1	6.8	6.0	171.9
-12	-13	1	10.3	10.4	173.7
-10	-13	1	15.7	16.2	231.1
-6	-13	1	22.8	26.3	169.6
-4	-13	1	15.9	17.1	192.8
-2	-13	1	17.9	19.0	137.3
0	-13	1	8.5	7.7	1.5
2	-13	1	25.3	20.8	293.9
4	-13	1	21.9	23.4	168.9
6	-13	1	16.1	16.2	209.0
8	-13	1	11.4	12.1	212.9
10	-13	1	10.0	9.2	220.0
12	-13	1	6.5	6.9	204.1
-9	-12	1	10.2	11.0	235.5
-7	-12	1	18.9	19.7	3.9
-5	-12	1	27.9	31.9	193.4
-3	-12	1	32.5	32.7	163.2
-1	-12	1	26.3	26.7	300.5
1	-12	1	40.9	43.9	252.3
3	-12	1	22.5	22.7	244.8
5	-12	1	20.3	21.9	170.5
7	-12	1	28.6	30.5	228.5
9	-12	1	17.0	16.2	358.6
11	-12	1	11.2	11.2	199.7
-10	-11	1	10.2	7.9	332.9
-8	-11	1	19.5	17.8	296.0
-6	-11	1	23.7	24.4	83.4
-4	-11	1	13.1	10.8	19.4
-2	-11	1	10.1	8.8	137.6
0	-11	1	23.1	21.2	354.9
2	-11	1	18.5	20.4	275.6
4	-11	1	21.2	21.9	212.2
8	-11	1	18.1	15.6	239.5
10	-11	1	16.2	15.8	16.8
-9	-10	1	21.2	21.7	350.4
-7	-10	1	34.3	35.4	1.2
-5	-10	1	30.2	30.9	54.1
-3	-10	1	35.1	37.6	102.9
-1	-10	1	24.0	25.2	0.9
1	-10	1	57.8	50.2	359.9
3	-10	1	22.7	25.7	130.6
5	-10	1	7.8	6.6	318.9
7	-10	1	16.5	15.7	53.8
9	-10	1	18.7	19.6	9.0
-8	-9	1	44.0	41.7	350.7
-6	-9	1	20.6	19.5	30.4
-4	-9	1	48.8	49.7	179.1
-2	-9	1	25.5	26.2	16.4

h	k	l	$\vert F_o\vert$	$\vert F_c\vert$	ϕ
0	-9	1	16.0	13.9	117.8
2	-9	1	45.2	43.7	341.1
4	-9	1	28.6	30.5	17.6
6	-9	1	39.3	44.2	77.5
8	-9	1	33.0	31.6	13.0
-7	-8	1	26.4	27.1	37.1
-5	-8	1	47.3	46.4	113.0
-3	-8	1	46.2	46.2	75.2
-1	-8	1	55.1	58.1	44.7
1	-8	1	33.4	31.1	304.1
3	-8	1	47.6	53.5	96.4
5	-8	1	34.6	31.5	85.4
7	-8	1	4.3	3.9	301.3
-6	-7	1	40.7	46.8	46.1
-4	-7	1	13.9	14.6	85.0
-2	-7	1	13.9	10.9	97.6
0	-7	1	45.9	45.1	103.0
2	-7	1	60.1	61.6	327.2
4	-7	1	68.2	67.4	142.1
6	-7	1	16.2	13.0	76.8
-5	-6	1	62.9	60.9	234.6
-3	-6	1	108.4	102.1	204.3
-1	-6	1	63.9	63.8	311.4
1	-6	1	45.7	39.9	268.9
3	-6	1	13.2	10.2	119.6
5	-6	1	20.5	18.6	13.5
-4	-5	1	90.6	86.4	198.8
-2	-5	1	59.4	55.8	217.6
0	-5	1	33.2	32.7	1.3
2	-5	1	84.1	81.7	227.7
4	-5	1	30.3	31.6	205.4
-3	-4	1	12.3	9.7	194.1
-1	-4	1	81.7	73.8	247.8
1	-4	1	18.2	18.5	236.9
3	-4	1	91.0	76.7	153.0
-2	-3	1	51.4	44.0	251.2
0	-3	1	78.7	73.7	341.2
2	-3	1	58.2	48.9	88.6
-1	-2	1	73.0	74.4	81.2
1	-2	1	52.3	44.1	208.3
-1	-19	2	7.3	6.8	43.3
3	-19	2	7.0	7.0	66.7
4	-18	2	8.2	7.0	73.8
-2	-18	2	10.5	10.2	104.8
4	-18	2	9.1	9.1	95.6
-3	-17	2	8.2	6.9	112.5
-1	-17	2	9.7	8.6	74.8
3	-17	2	8.2	8.6	53.5
5	-17	2	12.8	12.2	103.7
-8	-16	2	7.6	6.3	277.8
-2	-16	2	7.4	5.0	162.5
0	-16	2	16.6	14.9	340.7
4	-16	2	11.3	12.0	75.2
-9	-15	2	6.5	5.8	281.9
-7	-15	2	14.3	12.5	309.2
-3	-15	2	9.4	7.6	161.0
-1	-15	2	13.4	11.7	250.7
1	-15	2	7.7	6.9	283.2
3	-15	2	9.4	8.6	208.0
5	-15	2	9.2	9.5	124.5
-12	-14	2	9.1	7.4	180.4
-10	-14	2	12.6	12.5	280.8
-8	-14	2	11.6	11.6	284.9
-6	-14	2	12.1	11.4	312.7
-2	-14	2	17.5	17.0	168.4
0	-14	2	12.4	11.3	250.5
2	-14	2	12.4	13.0	270.5
4	-14	2	11.0	10.7	179.1
6	-14	2	5.4	6.2	242.5
10	-14	2	9.5	7.9	251.6
-9	-13	2	16.7	16.4	265.7
-7	-13	2	7.8	7.5	332.1
-5	-13	2	12.4	12.3	192.7
-3	-13	2	13.5	13.3	129.4
1	-13	2	33.0	32.1	260.9
3	-13	2	16.6	16.4	267.0
7	-13	2	20.6	19.2	249.9
9	-13	2	12.4	12.6	208.6
11	-13	2	11.9	10.8	237.0
-12	-12	2	8.5	6.5	135.0
-8	-12	2	11.1	10.7	295.6
-6	-12	2	9.6	10.0	143.0
-2	-12	2	17.0	14.3	218.7
0	-12	2	25.1	24.3	298.7
2	-12	2	30.0	31.7	274.7
4	-12	2	19.7	19.7	190.9
6	-12	2	9.6	9.7	184.7
8	-12	2	13.5	12.7	230.0
-11	-11	2	7.6	6.6	195.7
-9	-11	2	20.0	19.1	207.4
-7	-11	2	11.0	11.1	37.0
-5	-11	2	17.0	15.7	144.3
-3	-11	2	18.9	18.7	97.3
1	-11	2	24.1	25.7	274.0
3	-11	2	14.8	14.1	205.2
5	-11	2	20.8	22.2	182.9
7	-11	2	11.0	10.9	234.5
9	-11	2	13.6	13.3	317.5
-10	-10	2	13.6	13.4	12.2
-8	-10	2	11.0	7.8	309.3
-6	-10	2	15.0	15.5	70.3
-4	-10	2	30.4	29.4	70.6
-2	-10	2	22.5	22.5	84.6
0	-10	2	17.5	16.0	22.2
2	-10	2	26.5	27.4	327.3
6	-10	2	16.7	14.5	27.9
8	-10	2	9.5	7.1	332.4
-9	-9	2	10.9	8.5	327.0
-7	-9	2	12.8	13.2	13.7

h	k	l	$\vert F_o\vert$	$\vert F_c\vert$	ϕ
-5	-9	2	32.0	30.8	108.7
-3	-9	2	40.8	41.1	114.9
-1	-9	2	21.9	23.1	346.9
1	-9	2	27.4	27.1	15.4
3	-9	2	28.2	28.3	82.1
5	-9	2	42.0	42.1	75.2
7	-9	2	31.4	32.3	73.0
-8	-8	2	11.6	10.4	354.7
-6	-8	2	33.7	33.2	99.3
-4	-8	2	40.3	38.4	70.5
-2	-8	2	42.5	40.8	58.1
0	-8	2	12.7	14.8	67.0
2	-8	2	46.7	46.9	2.3
4	-8	2	34.3	35.3	119.3
6	-8	2	31.9	32.9	112.7
-7	-7	2	32.8	30.9	65.3
-5	-7	2	18.8	18.2	93.8
-3	-7	2	11.6	11.4	349.3
-1	-7	2	43.0	46.0	39.9
1	-7	2	45.8	45.3	299.1
3	-7	2	23.9	22.5	108.1
5	-7	2	31.0	32.0	125.0
-6	-6	2	39.0	41.4	256.8
-4	-6	2	33.7	33.0	205.6
-2	-6	2	26.7	28.5	227.1
0	-6	2	24.4	23.5	241.8
2	-6	2	13.7	14.3	269.2
4	-6	2	31.5	29.5	117.7
-5	-5	2	39.5	40.5	171.0
-3	-5	2	42.9	47.0	249.9
-1	-5	2	51.9	51.7	247.3
1	-5	2	44.9	52.2	260.8
3	-5	2	8.6	9.1	207.0
-4	-4	2	25.0	24.8	187.4
-2	-4	2	49.7	50.4	268.4
0	-4	2	56.0	56.0	279.0
2	-4	2	35.2	40.0	299.7
-3	-3	2	46.3	49.0	238.1
-1	-3	2	37.4	39.5	6.6
1	-3	2	26.0	26.7	78.5
-2	-2	2	12.0	13.3	86.8
0	-2	2	33.2	32.1	247.5
-1	-1	2	27.9	33.6	84.5
-9	-14	3	10.4	11.8	297.0
-7	-14	3	10.1	10.1	293.5
9	-14	3	9.0	8.5	291.8
-10	-13	3	9.3	9.7	310.1
-8	-13	3	13.5	13.3	287.9
0	-13	3	16.5	17.6	288.0
2	-13	3	16.5	17.2	279.9
10	-13	3	12.0	13.5	235.6
-3	-12	3	11.8	11.7	28.0
-1	-12	3	15.2	16.0	266.0
1	-12	3	21.5	21.1	267.3
3	-12	3	12.7	12.0	300.6
5	-12	3	11.7	9.4	119.0
11	-12	3	7.7	6.9	260.1
-8	-11	3	13.3	12.0	261.0
-6	-11	3	11.8	9.2	113.7
-4	-11	3	15.2	14.6	30.2
-2	-11	3	15.1	15.3	156.1
4	-11	3	13.6	12.9	149.8
6	-11	3	13.6	12.8	131.5
-5	-10	3	21.4	17.8	128.1
-3	-10	3	24.9	26.6	86.7
-1	-10	3	13.1	[illegible]	177.8
1	-10	3	12.3	[illegible]	332.6
3	-10	3	11.5	[illegible]	133.6
5	-10	3	11.6	10.3	[illegible]
-6	-9	3	11.6	10.5	[illegible]
-4	-9	3	27.6	25.6	[illegible]
-2	-9	3	16.7	16.3	[illegible]
0	-9	3	14.7	14.3	[illegible]
2	-9	3	17.0	15.1	[illegible]
4	-9	3	14.5	13.4	[illegible]
6	-9	3	31.4	31.3	68.4
-7	-8	3	15.7	14.4	141.6
-5	-8	3	23.0	23.4	102.6
-3	-8	3	28.7	30.8	53.7
-1	-8	3	13.3	13.0	72.1
1	-8	3	14.5	13.1	317.6
3	-8	3	25.9	26.7	76.0
5	-8	3	28.6	28.2	108.5
7	-8	3	22.1	20.4	123.2
-6	-7	3	9.0	8.3	360.0
-4	-7	3	25.2	23.9	73.9
0	-7	3	13.5	12.9	205.1
2	-7	3	21.8	22.4	344.1
4	-7	3	32.0	33.5	155.0
6	-7	3	[illegible]	8.4	105.6
-5	-6	3	13.1	13.5	247.4
-1	-6	3	19.8	19.3	306.6
1	-6	3	15.4	15.3	243.6
3	-6	3	26.4	26.0	[illegible]
5	-6	3	24.8	26.3	162.3
-4	-5	3	16.6	17.0	156.5
-2	-5	3	10.7	11.3	257.6
0	-5	3	26.5	27.3	[illegible]
2	-5	3	32.2	31.3	[illegible]
-3	-4	3	76.6	16.7	312.6
-1	-4	3	37.3	[illegible]	262.5
1	-4	3	[illegible]	56.3	[illegible]
3	-4	3	[illegible]	[illegible]	329.8
-2	-3	3	11.0	11.0	261.2
0	-3	3	41.8	48.5	300.8
2	-3	3	23.3	[illegible]	69.5
-1	-2	3	19.7	20.4	[illegible]
1	-2	3	16.4	17.8	233.1

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* Since the interlayer scale factors have been refined, it is necessary to multiply these values (which are on an absolute scale) by 1.771, 1.632, 1.428 and 1.048 for *h k* 0, *h k* 1, *h k* 2 and *h k* 3 for use in the weighting scheme.

TABLE 2

ATOM COORDINATES AND ISOTROPIC VIBRATIONAL AMPLITUDES ($Å^2 \times 10^3$) WITH ESTIMATED STANDARD DEVIATIONS*

Atom	x/a	y/b	z/c	U
N(1)	0.9372 (4)	0.0701 (5)	−0.1482 (17)	55 (2)
O	0.8174 (4)	0.0195 (4)	0.1696 (14)	65 (2)
N(2)	0.7552 (5)	0.0621 (4)	0.0328 (16)	55 (2)
C(1)	0.6841 (7)	0.0123 (6)	0.0476 (29)	72 (3)
C(2)	0.7489 (7)	0.1402 (7)	0.1724 (30)	71 (3)

* The Zachariasen secondary extinction coefficient refined to the value 14.4 (1.6) × 10^{-6}.

TABLE 3

ATOM COORDINATES AND ANISOTROPIC VIBRATIONAL AMPLITUDES ($Å^2 \times 10^3$) WITH ESTIMATED STANDARD DEVIATIONS

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	0.8865 (1)	−0.0057 (1)	−0.0819 (6)	54 (1)	59 (1)	68 (4)	3 (1)	−1 (1)	−2 (1)
F(1)	0.6274 (4)	0.0471 (5)	−0.0895 (26)	76 (4)	111 (5)	149 (7)	−3 (6)	−11 (5)	13 (3)
F(2)	0.6612 (5)	−0.0055 (5)	0.2955 (20)	126 (7)	125 (6)	124 (9)	28 (5)	51 (5)	−23 (5)
F(3)	0.7013 (4)	−0.0552 (4)	−0.0829 (22)	82 (4)	79 (4)	158 (7)	−23 (5)	−8 (5)	−8 (3)
F(4)	0.8155 (5)	0.1784 (4)	0.1283 (29)	99 (5)	83 (4)	222 (9)	−39 (6)	35 (6)	−13 (4)
F(5)	0.6906 (4)	0.1797 (4)	0.0483 (22)	97 (5)	86 (4)	153 (8)	25 (5)	12 (5)	23 (3)
F(6)	0.7368 (6)	0.1388 (5)	0.4326 (22)	167 (8)	102 (5)	95 (8)	−24 (5)	23 (6)	25 (5)

TABLE 4

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEGREES)

S–N(1)	1.56 (1)	S–N(1)′	1.62 (1)
S–O	1.71 (1)	O–N(2)	1.42 (1)
N(2)–C(1)	1.46 (2)	N(2)–C(2)	1.47 (2)
C(1)–F(1)	1.29 (2)	C(1)–F(2)	1.27 (2)
C(1)–F(3)	1.32 (2)	C(2)–F(4)	1.30 (2)
C(2)–F(5)	1.32 (2)	C(2)–F(6)	1.25 (2)
N(1)–S–N(1)′	111.8 (0.5)	S–N(1)–S′	123.4 (0.4)
N(1)–S–O	107.9 (0.4)	N(1)′–S–O	88.9 (0.4)
S–O–N(2)	107.6 (0.5)	O–N(2)–C(1)	106.9 (0.7)
O–N(2)–C(2)	107.2 (0.7)	C(1)–N(2)–C(2)	115.4 (0.9)
N(2)–C(1)–F(1)	109 (1)	N(2)–C(1)–F(2)	115 (1)
N(2)–C(1)–F(3)	107 (1)	F(1)–C(1)–F(2)	110 (1)
F(2)–C(1)–F(3)	107 (1)	F(3)–C(1)–F(1)	108 (1)
N(2)–C(2)–F(4)	108 (1)	N(2)–C(2)–F(5)	108 (1)
N(2)–C(2)–F(6)	116 (1)	F(4)–C(2)–F(5)	108 (1)
F(5)–C(2)–F(6)	109 (1)	F(6)–C(2)–F(4)	115 (1)

TABLE 5

SHORTEST NON-BONDED DISTANCE (Å)

I Within the same asymetric unit	
Six F–F within same CF_3 group	2.06–2.12
Six N(2)–F	2.23–2.31
O–C(1), O–C(2)	2.31, 2.32
C(1)–C(2)	2.47
S–N(2)	2.53
F(1)–F(5)	2.54
O–F(3), O–F(4), O–F(6), O–F(2)	2.60–2.71
N(1)–O	2.65
F(2)–F(6)	2.80
C(1)–F(5), C(2)–F(1), C(2)–F(2), C(1)–F(6)	2.80–2.93
N(1)–F(4)	3.02
N(1)–N(2)	3.17
II Other intramolecular distances	
N(1)–O	2.33
N(1)–N(1)′	2.63 and 3.15
S–S	2.80
F(3)–F(4)	2.96
S–N(1)	3.15
III Intermolecular distances	
F(5)–F(6)	3.09
F(1)–F(2)	3.09
F(4)–F(5)	3.10
F(1)–F(2)	3.12
F(2)–F(3)	3.13
N(2)–F(6)	3.13

factors[7, 8] were employed for all atoms. The final value of

$$R_\omega = \Sigma\, \omega^{1/2} \big|\, |F_0| - |F_c| \,\big| / \Sigma\, \omega^{1/2} |F_0|$$

was 0.074 for a total of 436 unique observed reflections; the corresponding unweighted "R index" was 0.066. A final difference Fourier analysis revealed no pronounced features. Observed and calculated factors are shown in Table 1, and the results from the final full-matrix least-squares cycle are given in Tables 2 and 3. These results, together with the full covariance matrix and the estimated standard deviations in the unit-cell dimensions, were used to calculate the bond lengths and angles given in Tables 4 and 5; no corrections have been applied for libration. Figure 1 shows the structure in projection down the Z axis.

DISCUSSION

The geometry of the $N_4S_4O_4$ moiety is remarkably similar to that of $N_4S_4F_4$[4] (S–N = 1.66 and 1.54 Å, < N–S–N = 111.7°, < S–N–S = 123.9°, < N–S–F = 91.5° and 106.2°). A significant alternation in the S–N bond lengths is found in

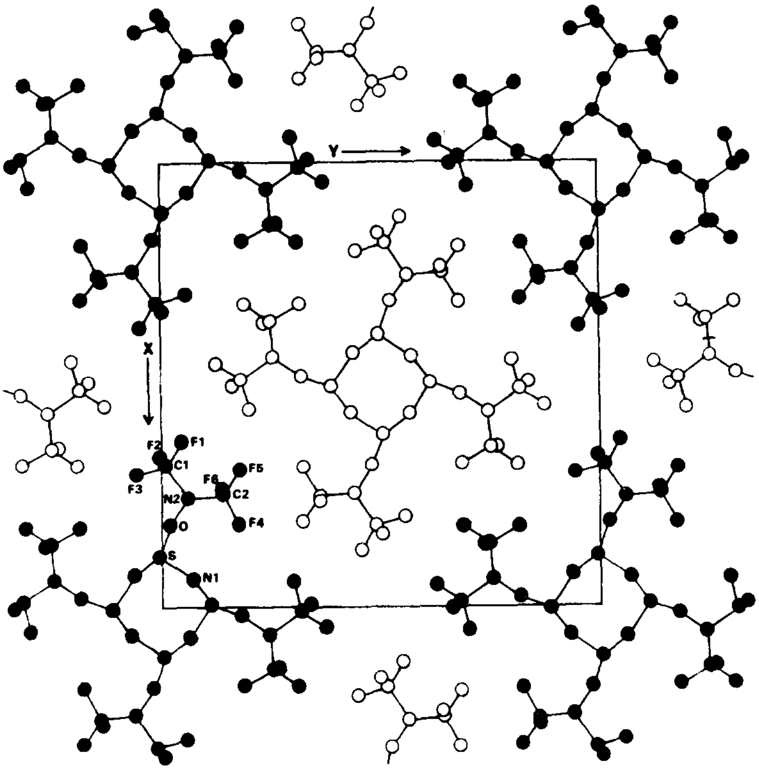

Fig. 1. The crystal structure seen in projection down the *Z* axis.

both compounds, and implies appreciable localisation of N–S $p\pi$–$d\pi$ bonding. The stereochemistry at sulphur atom is consistent with the Nyholm–Gillespie hypothesis[9] of electron pair repulsions (Fig. 2), if it is assumed that there is one lone pair of elections on the sulphur atom; as expected, the wider N–S–O angle involves the shorter N–S bond. The N–O and S–O bond lengths appear to be consistent with "single" bonds, although it is difficult to find suitable reference

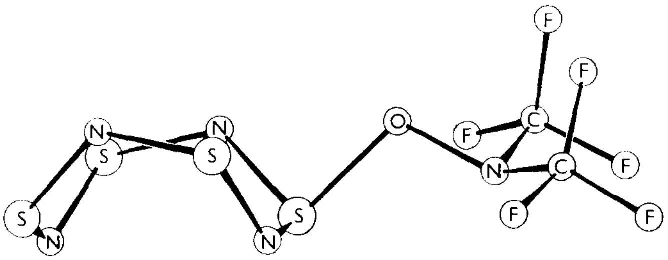

Fig. 2. The molecule of tetrathiazyl tetra [bis-(trifluoromethyl) nitroxide], showing one of the bis-(trifluoromethyl) nitroxide substituents.

compounds. The $ON(CF_3)_2$ dimensions are similar to those in the free radical[10], except that the N–O bond is longer, and the angles at the nitrogen atom are closer to the tetrahedral values. The CF_3 groups are staggered with respect to the C–N bonds, as found for the free radical.

The non-bonded distances are given in Table 5. The packing can be compared with that in $N_4S_4F_4$ (space group $P\bar{4}2_1c$, $a = 9.19$, $c = 4.30$ Å)[4]. All the shortest intermolecular contacts in $[NSON(CF_3)_2]_4$ are between fluorine atoms, which would tend to push the $[NS]_4$ rings apart, resulting in a longer Z axis than in $N_4S_4F_4$.

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