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The Crystal Structure of $S_4N_4H_4$*

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A three-dimensional X-ray study of crystalline $S_4N_4H_4$ shows that it is orthorhombic with a = 8·010, b = 12·20, c = 6·727 Å, Z = 4, and space group D_{2h}^{16}–$Pnma$. The approximate structure, as obtained from the Patterson function, was refined by Fourier and least-squares methods. The molecule is a puckered eight-membered ring of alternating sulfur and nitrogen atoms. Packing considerations indicate N–H bonds, rather than S–H bonds, in agreement with spectroscopic studies. The S–N bond length is 1·674±0·004 Å. The dihedral angle, S–N–S–N, is 99·4°. The bond angles are S–N–S = 122·2° and N–S–N = 108·4°. The required molecular symmetry is C_s–m, but is C_{4v}–$4mm$ within the accuracy of the results. The S–N bond type is discussed relative to S_4N_4 and other compounds containing S–N bonds. There is evidence for a weak N–H · · · N hydrogen bond of length 3·16 Å.

Introduction

Although $S_4N_4H_4$ has been actively investigated since 1908, its molecular structure has remained unresolved. The substance is prepared by reducing sulfur nitride, S_4N_4, with alcoholic stannous chloride (Wöbling, 1908). Molecular weight determinations in acetone (Meuwsen, 1929) show the compound to be the tetramer. The substance is a crystalline solid, stable in air and moisture, which decomposes over a temperature range from 100° C. to about 148° C. It is attacked only slowly by acids and alkalies, even in fairly strong concentration. It is appreciably soluble in acetone, piperidine, and pyridine, but insoluble in most other solvents.

$S_4N_4H_4$ is prepared directly from S_4N_4, and it has been generally assumed that the structures of both are similar. Electron-diffraction studies (Lu & Donohue, 1944) on gaseous S_4N_4 and two-dimensional X-ray diffraction studies (Clark, 1952) on the solid phase agree that the molecule is a cage made up of a square of nitrogen atoms and a bisphenoid of sulfur atoms. There is, though, a second electron-diffraction investigation of S_4N_4 which assigns a different cage structure consisting of a bisphenoid of nitrogen atoms and a square of sulfur atoms (Hassel & Viervoll, 1943). A study of the infra-red and Raman spectra (Lippincott & Tobin, 1953) of S_4N_4 also assigns this latter structure to the molecule. At the same time, Lippincott & Tobin studied the infra-red spectrum of solid $S_4N_4H_4$, and found that it was very similar to that of S_4N_4. They concluded that when $S_4N_4H_4$ is formed from S_4N_4, N–N bonds are broken and N–H bonds are formed. Their hypothesis is supported by the appearance of strong absorption peaks in the spectrum of $S_4N_4H_4$ at 3220, 3285 and 3320 cm.$^{-1}$, frequencies characteristic of N–H vibrations. Chemical evidence, on the other hand, regarding the location of the hydrogen atoms is conflicting. Arnold (1938) and Goehring (1947), on the basis of several reactions of $S_4N_4H_4$, favored a structure with four equivalent N–H bonds, while Meuwsen (1929) and Sidgwick (1950) preferred a structure with S–H bonds.

One previous X-ray diffraction study by Jaeger & Zanstra (1931) has been reported on $S_4N_4H_4$. These authors presented a structure which consists of two interpenetrating bisphenoids of sulfur and nitrogen atoms. They did, however, base their structure on an incorrect space group, thus invalidating their results.

In order to resolve the reported structure differences indicated above, the investigation of $S_4N_4H_4$ described below has been undertaken. The resulting structure will be discussed and compared with those already mentioned. We have also begun a three-dimensional X-ray study of S_4N_4, the results of which will be reported later.

Experimental

The unit cell and space group

$S_4N_4H_4$ was prepared by the method described by Meuwsen (1929). The crystals used in this investigation were obtained by slow evaporation of pyridine solutions. They were small needles, colorless and slightly milky in appearance. Weissenberg photographs showed the crystals to be orthorhombic. Values of the lattice constants, as obtained from rotation photographs around the three crystallographic axes, are:

$$a=8{\cdot}010\pm0{\cdot}010,\quad b=12{\cdot}20\pm0{\cdot}014,\quad c=6{\cdot}727\pm0{\cdot}009\text{ Å}$$
$$(\lambda \text{ for Cu } K\alpha = 1{\cdot}5418\text{ Å})\,.$$

The axial ratios $a:b:c$ = 0·656:1:0·552 compare with the goniometric values of 0·644:1:0·549 reported by Jaeger & Zanstra (1931).

Weissenberg photographs were recorded around $a(h = 0\text{–}5)$ and $c(l = 0\text{–}4)$ from two different crystals, each about 0·2×0·2×0·3 mm. The systematic absence

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of ($hk0$) reflections with h odd and of ($0kl$) reflections with $k+l$ odd allowed two possible space groups, the hemihedral space group C_{2v}^9–$Pn2a$ (No. 33), or the holohedral space group D_{2h}^{16}–$Pnma$ (No. 62). The density of the crystal calculated on the basis of four molecules per cell is 1·90 g.cm.$^{-3}$ compared with the experimental density of 1·88 g.cm.$^{-3}$ as determined pycnometrically with carbon tetrachloride. Thus, if the crystal is centrosymmetric, the molecule must possess either a center of symmetry or a mirror plane.

Of the 917 non-equivalent reflections in the sphere of reflection, 125 were extinguished by the space group, 65 were not recorded on the photographs taken, 213 were too weak to observe and 514 were observed. Intensities were estimated by the multiple-film technique and an intensity strip. The standard error in an observed F_{hkl} is about 3·5%, as judged by the internal consistency of the estimated intensities of reflections occurring on more than one Weissenberg photograph. No absorption corrections were made. The relative values of F_{hkl}^2 were placed on an approximately absolute scale and an average isotropic temperature factor was determined by the method of Wilson (1942).

The intensity distribution curve (Wilson, 1949; Howells, Phillips & Rogers, 1950; Lipson & Woolfson, 1952) for $S_4N_4H_4$, shown in Fig. 1, was found to lie between the theoretical curves for a centric and a hypercentric structure. Thus the space group of $S_4N_4H_4$ is the centrosymmetric D_{2h}^{16}–$Pnma$. It may also be inferred that the structure, although not being quite hypercentric, possesses groups of atoms which are related by centers of symmetry other than those of the space group.

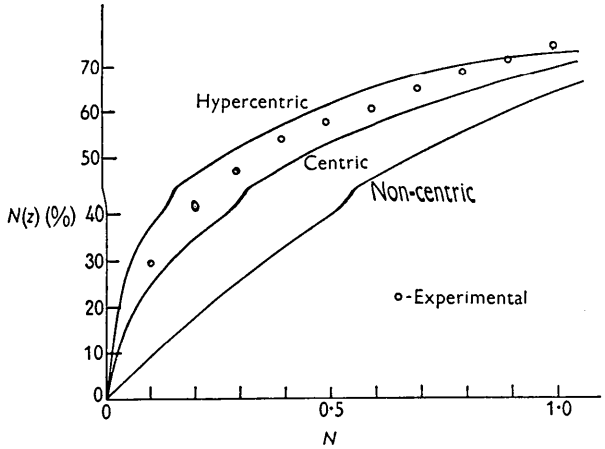

Fig. 1. Intensity distribution curves.

Determination of trial structure

In order to obtain a trial structure for $S_4N_4H_4$, a three-dimensional Patterson function was calculated. To increase the resolution of this function the coefficients were sharpened and the peak at the origin was removed (Patterson, 1935; Waser, 1944; Waser & Schomaker, 1953). The unmodified Patterson function was also computed. These computations were carried out on the National Bureau of Standards Western Automatic Computer (SWAC) at the University of California at Los Angeles (Sparks, Prosen, Kruse & Trueblood, 1956). Since the resolution of the modified Patterson was slightly better than that of the unmodified function, and since there were no serious differences between the two, the modified Patterson function was used exclusively to determine the trial structure.

The interpretation of the Patterson function was initiated by considering the various Harker sections and lines. Several possible heavy-atom positions were found, one of which, together with its seven equivalents generated by the space group, was used to make a vector convergence plot (Beevers & Robertson, 1950), a method which is unusually well suited for this structure for a number of reasons: A large number of the Patterson peaks in the unit cell were very well resolved, and it was hoped that a detailed consideration of the Patterson function would result in much better parameters than would have been obtained by trial and error methods; also, the presence of the heavier sulfur atoms reduced the observed complexity of the Patterson function, since the sulfur–sulfur and sulfur–nitrogen interactions completely overshadowed the weaker nitrogen–nitrogen interaction peaks; finally, the vector convergence method, as applied here, did not require any assumptions concerning the shape or size of the molecule.

There were only five eightfold overlaps in the asymmetric unit of the vector convergence plot. Two of these corresponded to probable positions of sulfur atoms already found from the Harker sections, and the three other overlaps were assumed to be at the centers of nitrogen atoms. A trial structure based on these assumptions led to an $S_4N_4H_4$ molecule consisting of an eight-membered puckered ring of alternating sulfur and nitrogen atoms. The molecule lay across a mirror plane in the crystal, and contained two crystallographically independent sulfur atoms and three crystallographically independent nitrogen atoms. The interatomic bond distances and bond angles based on this trial structure were not chemically unreasonable, and the distances between atoms of neighboring molecules were all 3·2 Å or more. The interatomic vectors for this trial structure were calculated and compared with the observed Patterson function. The fit was highly satisfactory, and the position and shape of every peak was explained. From this fit it could be assumed with certainty that the trial structure was correct, except for small errors in atomic positions, probably less than 0·1 Å.

Refinement of the structure

The refinement of the trial structure obtained from the interpretation of the Patterson vector map was

Table 1. *Atomic parameters and progress of refinement*

Atom	Patterson trial structure	Fourier projections	Fifth least squares	Final least squares	Final Fourier	Final parameters	σ (least squares)
S_1 x	0·042	0·037	0·0413	0·0415	0·0415	0·0415	0·0004
y	0·129	0·129	0·1298	0·1299	0·1300	0·1300	0·0002
z	0·179	0·176	0·1809	0·1810	0·1809	0·1810	0·0004
S_2 x	0·125	0·130	0·1371	0·1372	0·1371	0·1372	0·0003
y	0·129	0·129	0·1304	0·1303	0·1304	0·1304	0·0002
z	0·750	0·747	0·7568	0·7571	0·7578	0·7575	0·0004
N_1 x	0·212	0·212	0·2326	0·2329	0·2320	0·2325	0·0016
y	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	
z	0·733	0·733	0·7191	0·7191	0·7193	0·7192	0·0016
N_2 x	0·108	0·108	0·1118	0·1117	0·1112	0·1115	0·0020
y	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	
z	0·250	0·250	0·2702	0·2710	0·2724	0·2717	0·0019
N_3 x	0·158	0·169	0·1678	0·1678	0·1675	0·1677	0·0012
y	0·080	0·091	0·0924	0·0924	0·0926	0·0925	0·0008
z	0·983	0·993	0·9948	0·9944	0·9936	0·9940	0·0014
R	—	28·9	12·0	—	—	11·8	—
$\Sigma w(\Delta F)^2$	—	8910	1586	—	—	—	—

carried out by three-dimensional Fourier and least-squares treatments, preceded by preliminary Fourier refinements of the $(0kl)$ and $(h0l)$ prism zones. The least-squares calculations were made on the SWAC (Sparks *et al.*, 1956); a total of 514 observational equations was used. The five atoms in the asymmetric unit generated 13 normal equations for the shifts in the positional parameters and 26 normal equations for the shifts in the thermal vibration parameters, plus the normal equation for the change in the scale factor. The weighing system used was

$$\sqrt{w} = 4F_{\text{min.}}/F_o \quad \text{for} \quad F_o \geq 4F_{\text{min.}} \quad \text{and}$$
$$\sqrt{w} = F_o/4F_{\text{min.}} \quad \text{for} \quad F_o < 4F_{\text{min.}}$$

The initial values of the positional parameters used were those obtained from the two-dimensional Fourier syntheses. The temperature factors of all atoms were assumed initially to be isotropic and equal in magnitude to the value obtained from the Wilson plot.

A total of six cycles of least squares was then calculated. After each cycle the indicated shifts in the parameters were divided by 2 and added to the previous values of the parameters. In the first cycle the value of the reliability index was reduced from 28·9% to 20·1%, and then dropped steadily to a final value of 11·8%. The sum of the residuals, $\Sigma w(\Delta F)^2$, was reduced in the first cycle of least squares by a factor of about 0·6, and finally dropped to about 18% of the original value. The initial scale factor obtained from the Wilson plot was found to differ by less than 10% from the final value obtained from the least-squares refinement. Some of the values of the atomic parameters during the progress of the structure refinement are given in Table 1. The final shifts in all parameters are seen to be smaller than the standard deviations of the corresponding parameters. The initial and final values of the temperature-factor parameters are listed in Table 2. These have been multiplied by the appropriate constants such that they can be

Table 2. *Temperature-factor parameters, β_{ij}*

Atom	β_{ij}	Initial values	First least squares	Final least squares
S_1	11	3·1 Å^2	3·8 Å^2	5·0 Å^2
	22	3·1	3·4	3·4
	33	3·1	2·9	2·1
	12	0·0	−0·2	−0·5
	23	0·0	0·2	0·9
	31	0·0	0·6	1·3
S_2	11	3·1	3·5	3·3
	22	3·1	3·0	2·9
	33	3·1	2·9	2·0
	12	0·0	0·4	0·5
	23	0·0	0·4	0·1
	31	0·0	−0·4	−1·0
N_1	11	3·1	3·5	2·8
	22	3·1	3·6	4·2
	33	3·1	3·0	1·2
	31	0·0	−2·0	0·4
N_2	11	3·1	2·9	5·7
	22	3·1	3·7	3·8
	33	3·1	3·5	1·0
	31	0·0	−1·3	−0·3
N_3	11	3·1	3·7	4·1
	22	3·1	4·0	3·4
	33	3·1	2·2	2·0
	12	0·0	0·4	0·5
	23	0·0	0·1	0·2
	31	0·0	0·3	0·3

Table 3. *Peak heights in Fourier syntheses*

Atom	Max. in ϱ_o (e.Å^{-3})	Max. in ϱ_c (e.Å^{-3})	ϱ_c/ϱ_o
S_1	29·7	30·5	1·03
S_2	33·2	34·7	1·04
N_1	9·9	10·2	1·03
N_2	8·9	9·6	1·08
N_3	9·6	9·7	1·01

compared to the usual values reported for isotropic temperature factors with dimensions Å². An interpretation of these values in terms of the ellipsoids of vibration is given below.

Additional refinement of the structure was next obtained by three-dimensional Fourier methods. Two three-dimensional Fourier syntheses were prepared, one using structure factors calculated from the set of parameters obtained from the final least-squares refinement (Table 1), and the other with the observed magnitudes of the structure factors and phases determined from the calculated structure factors. In both cases, only those planes having a non-zero value for the observed intensity were included. These computations were also carried out on the SWAC. Both syntheses were evaluated at intervals of sixtieths along all three axes. The positions of the maxima in the observed and calculated electron-density functions were calculated on the assumption that the peaks can be represented by Gaussian ellipsoids (Shoemaker, Donohue, Schomaker & Corey, 1950). The nineteen points nearest each maximum (Donohue & Trueblood, 1952) were used in an analytical method involving least squares. A full back-shift correction was applied to the observed peak maxima to obtain parameters corrected for series termination. The average back-

Table 4. *Observed and calculated structure factors*

(all F's have been multiplied by 10)

h	k	F_o	F_c
$\ell = 0$			
0	2	449	427-
0	4	997	1595-
0	6	296	194-
0	8	966	1082
0	10	242	236-
0	12	383	373-
0	14	139	109
2	0	175	296
2	1	742	1433-
2	2	49	43
2	3	773	858-
2	4	510	513-
2	5	542	601
2	6	261	241
2	7	586	618
2	8	246	244
2	9	479	494-
2	10	64	71-
2	11	166	150-
2	12	202	189-
2	13	216	216
2	14	63	58
2	15	73	60
4	0	354	409-
4	1	98	89-
4	2	29	39-
4	3	<29	35-
4	4	329	338
4	5	217	212
4	6	45	16
4	7	52	30
4	8	193	179-
4	9	175	164-
4	10	<53	9
4	11	62	57-
4	12	90	91
4	13	79	90
4	14	<29	29-
6	0	224	218
6	1	51	28
6	2	69	88
6	3	<59	29
6	4	274	280-
6	5	<61	33-
6	6	<63	30
6	7	<62	19-
6	8	<61	62
6	9	<57	31
6	10	<52	12
6	11	<45	13
6	12	<36	45-
8	0	148	129
8	1	201	185-
8	2	45	55-
8	3	269	236-
8	4	52	56-
8	5	232	214
8	6	46	11
8	7	111	86
8	8	125	98
8	9	150	100-
10	0	211	161-
10	1	142	102-
10	2	<31	10
10	3	<26	32-
$\ell = 1$			
0	1	86	82
0	3	75	73
0	5	95	65-
0	7	50	36-
0	9	<59	51
0	11	<63	22
0	13	<57	46-
0	15	<36	6-
1	0	576	660
1	1	239	250-
1	2	100	90
1	3	480	445-
1	4	476	460-
1	5	50	54
1	6	59	58-
1	7	178	151
1	8	198	185
1	9	72	59
1	10	<62	19
1	11	<63	46-
1	12	79	80-
1	13	<56	15-
1	14	<49	15
1	15	<36	9-
2	0	266	371
2	1	560	815-
2	2	122	96
2	3	257	276-
2	4	482	490-
2	5	316	354
2	6	138	133
2	7	325	313
2	8	201	200
2	9	349	365-
2	10	<62	39-
2	11	69	54-
2	12	166	154-
2	13	148	142
2	14	54	66
2	15	45	38-
3	0	89	80-
3	1	146	163-
3	2	140	136-
3	3	109	119-
3	4	39	11
3	5	131	114
3	6	178	165
3	7	109	84
3	8	114	105
3	9	90	82-
3	10	113	100-
3	11	49	39-
3	12	81	84-
3	13	40	42
3	14	<31	25
4	0	661	703-
4	1	305	418-
4	2	105	114
4	3	512	649-
4	4	426	463
4	5	572	663
4	6	60	47-
4	7	190	186
4	8	348	369-
4	9	287	311-
4	10	120	117
4	11	180	168-
4	12	148	155
4	13	284	241
4	14	61	55-
5	0	104	123
5	1	<22	26-
5	2	<22	23
5	3	<27	14
5	4	81	87-
5	5	119	124
5	6	51	34-
5	7	<41	10-
5	8	<43	26
5	9	117	107-
5	10	<41	15
5	11	<39	24-
5	12	<33	2
5	13	76	61
6	0	532	566-
6	1	113	103
6	2	<63	32-
6	3	120	133
6	4	704	623
6	5	142	144-
6	6	139	141-
6	7	61	45-
6	8	335	340-
6	9	63	76
6	10	57	65
6	11	<50	34
6	12	160	225
7	0	68	38
7	1	125	111-
7	2	<68	8
7	3	122	105-
7	4	<68	11-
7	5	<66	40
7	6	<65	29-
7	7	69	75
7	8	<59	1-
7	9	<53	17-
7	10	<45	9
7	11	<33	17-
8	0	<65	1
8	1	203	199
8	2	<64	12
8	3	162	153
8	4	<63	31-
8	5	163	167-
8	6	<56	21
8	7	121	115-
8	8	<45	2
8	9	154	131
9	0	82	70-
9	1	<55	25-
9	2	<54	7-
9	3	<52	26-
9	4	<50	41
9	5	<45	27
9	6	<40	30
9	7	<31	13
10	0	82	76
10	1	<35	43-
10	2	<31	14-
$\ell = 2$			
0	0	960	1491-
0	2	563	583
0	4	640	729
0	6	188	213-
0	8	780	844-
0	10	355	366
0	12	371	363
0	14	138	117-
1	0	159	117-
1	1	331	385-
1	2	44	53
1	3	294	340-
1	4	45	42
1	5	333	358
1	6	<49	12-
1	7	162	162
1	8	81	59-
1	9	226	213-
1	10	<63	30
1	11	98	83-
1	12	<60	18
1	13	139	119
1	14	<44	6-
1	15	<29	23
2	0	352	339-
2	1	676	777
2	2	143	145-
2	3	189	211
2	4	367	411
2	5	511	564-
2	6	54	28-
2	7	296	305-
2	8	115	103-
2	9	504	561
2	10	<63	25-
2	11	118	101
2	12	84	67
2	13	245	258-
2	14	<41	30-
3	0	224	226-
3	1	308	295-
3	2	52	53-
3	3	238	261-
3	4	281	305
3	5	231	240
3	6	79	75-
3	7	158	157
3	8	131	131-
3	9	167	155-
3	10	<49	13
3	11	79	76-
3	12	96	95
3	13	86	85
3	14	<26	30-
4	0	266	289
4	1	188	161
4	2	54	45-
4	3	203	221
4	4	274	294-
4	5	79	54-
4	6	113	100
4	7	123	111-
4	8	236	235
4	9	<53	16-
4	10	71	71-
4	11	<56	33
4	12	157	150-
4	13	<35	9
5	0	335	365-
5	1	105	104-
5	2	46	33
5	3	45	30-
5	4	263	267
5	5	61	46
5	6	<40	2
5	7	68	54
5	8	203	206-
5	9	73	62-
5	10	44	30
5	11	<36	8-
5	12	110	97
5	13	<22	20
6	0	<64	4
6	1	101	107-
6	2	<65	4-
6	3	108	95-
6	4	121	131
6	5	118	97
6	6	159	153-
6	7	73	71
6	8	<64	59-
6	9	81	73-
6	10	69	59
6	11	<45	42-
6	12	92	84
7	0	173	153-
7	1	<69	56
7	2	<69	4
7	3	<69	33
7	3	<69	33
7	4	173	143
7	5	<66	19-
7	6	<64	22-
7	7	<61	46-
7	8	101	95-
7	9	<50	25
7	10	<41	16
8	0	178	191-
8	1	100	94
8	2	<63	30
8	3	119	109
8	4	111	104
8	5	181	186-
8	6	<54	26
8	7	<49	16-
8	8	107	105-
8	9	98	114
9	0	<52	44-
9	1	<52	25
9	2	<51	10
9	3	<49	34
9	4	<45	29
9	5	<41	34-
9	6	<35	7-
$\ell = 3$			
0	1	413	352-
0	3	271	305-
0	5	346	341
0	7	185	187
0	9	246	234-
0	11	112	112-
0	13	180	142
1	0	650	540-
1	1	98	60-
1	2	40	32
1	3	<29	56
1	4	505	576
1	5	267	250
1	6	191	168-
1	7	<57	36
1	8	359	376-
1	9	131	129
1	10	102	87
1	11	93	78
1	12	220	237
1	13	101	104-
1	14	59	55-
2	0	401	436-
2	1	290	290
2	2	46	41-
2	3	<45	7
2	4	400	523
2	5	63	95-
2	6	131	135-
2	7	108	101-
2	8	261	280-
2	9	164	170
2	10	<61	53
2	11	90	22-
2	12	189	196
2	13	59	52-
2	14	66	65-
3	0	540	537-
3	1	346	315
3	2	<36	8-
3	3	242	237
3	4	308	332
3	5	220	236-
3	6	80	76
3	7	168	179-
3	8	176	173-
3	9	183	173
3	10	<47	12
3	11	73	85
3	12	<40	33
3	13	102	85-
4	0	270	301
4	1	251	244
4	2	99	84-
4	3	395	398
4	4	182	178-
4	5	391	446-
4	6	51	47
4	7	107	97-
4	8	164	172
4	9	196	206
4	10	88	92-
4	11	113	110
4	12	70	64-
4	13	170	173-
5	0	69	14-
5	1	231	223
5	2	<36	32
5	3	250	264
5	4	<40	29
5	5	179	180-
5	6	76	68-
5	7	119	123-
5	8	<43	38-
5	9	84	74
5	10	62	52
5	11	54	45
5	12	<24	30
6	0	343	318
6	1	108	99-
6	2	<73	24
6	3	114	105-
6	4	373	376-
6	5	131	139
6	6	125	108
6	7	<70	36
6	8	182	194
6	9	96	86-
6	10	<52	49-
6	11	<40	27-
7	0	<73	17
7	1	118	120
7	2	<73	26
7	3	<72	27
7	4	<70	32-
7	5	105	107-
7	6	<65	7-
7	7	<61	46-
7	8	<54	12-
7	9	108	123
7	10	<31	15
8	0	88	75-
8	1	131	149-
8	2	<64	2-
8	3	105	113-
8	4	85	90
8	5	104	127
8	6	<52	29-
8	7	72	81
8	8	46	52-
9	0	<50	42
9	1	<50	55
9	2	<49	31-
9	3	<45	60
9	4	<40	17-
9	5	51	61-
$\ell = 4$			
0	0	1011	866
0	2	148	140-
0	4	366	397-
0	6	108	100-
0	8	346	352
0	10	120	116-
0	12	81	70-
1	0	182	128
1	1	310	328
1	2	57	38-
1	3	290	310
1	4	<55	34-
1	5	320	346-
1	6	<60	9-
1	7	120	130-
1	8	81	40
1	9	211	206
1	10	<62	32-
1	11	<56	58
1	12	<50	5
1	13	125	126-
2	0	329	309-
2	1	558	539-
2	2	52	18
2	3	333	335-
2	4	159	153
2	5	241	261
2	6	81	88
2	7	256	282
2	8	130	127-
2	9	226	241-
2	10	<59	10-
2	11	54	42-
2	12	<44	30
2	13	115	103
3	0	209	191
3	1	316	277
3	2	81	62
3	3	221	223
3	4	292	314-
3	5	265	267-
3	6	119	109
3	7	149	146-
3	8	109	111
3	9	202	189
3	10	<44	19-
3	11	81	79
3	12	94	100-
3	13	81	105-
4	0	439	520-
4	1	166	180
4	2	<49	4
4	3	205	198
4	4	397	437
4	5	95	85-
4	6	<53	18-
4	7	138	128-
4	8	253	281-
4	9	<50	32
4	10	61	44
4	11	53	43
4	12	134	143
5	0	313	387
5	1	144	119
5	2	76	60
5	3	53	21
5	4	281	273-
5	5	<43	29-
5	6	<43	15
5	7	75	65-
5	8	222	241
5	9	70	64
5	10	54	55-
5	11	<24	0
6	0	121	136
6	1	214	216
6	2	<93	56
6	3	209	180
6	4	199	169-
6	5	206	189-
6	6	<83	5
6	7	133	129-
6	8	<72	36
6	9	120	145
6	10	<49	18
7	0	167	166
7	1	<85	79-
7	2	<83	0
7	3	<83	37-
7	4	113	155-
7	5	<76	34
7	6	<72	22
7	7	91	63
7	8	102	95
8	0	133	144
8	1	<72	53-
8	2	<71	37-
8	3	109	90-
8	4	102	90-
8	5	<57	74
8	6	<49	9
9	0	<43	37
9	1	<43	31-
$\ell = 5$			
0	1	647	534
0	3	541	497
0	5	489	497-
0	7	297	297-
0	9	305	326
0	11	171	156
1	0	599	471
1	1	161	105-
1	2	60	42
1	3	316	320-
1	4	472	470-
1	5	192	171
1	6	63	51
1	7	90	94
1	8	224	234
1	9	<60	11
1	10	<54	22-
1	11	88	88-
1	12	156	136-
2	0	634	518
2	1	64	49
2	2	<59	26
2	3	160	143
2	4	493	535-
2	5	121	125-
2	6	93	87
2	7	<62	50-
2	8	277	303
2	9	<56	35
2	10	56	49-
2	11	70	72
2	12	196	191-
3	0	69	56
3	1	267	219-
3	2	117	106-
3	3	173	152-
3	4	<49	9-
3	5	183	168
3	6	96	109
3	7	118	117
3	8	83	86
3	9	114	137-
3	10	102	118-
3	11	44	49-
4	0	<53	0-
4	1	142	103-
4	2	<53	30
4	3	201	200-
4	4	49	49-
4	5	178	210
4	6	<52	2-
4	7	<50	35
4	8	<46	18
4	9	89	85-
4	10	<35	36
4	11	53	52-
5	0	69	58
5	1	<43	44-
5	2	<43	4
5	3	54	34-
5	4	<41	37-
5	5	141	142
5	6	<40	4-
5	7	36	27-
5	8	<33	4
5	9	108	99-
5	10	<22	7-
$\ell = 6$			
0	0	<63	10-
0	2	156	129
0	4	80	85-
0	6	82	66-
0	6	81	66-
0	8	<54	71-
0	10	148	120
1	0	63	17
1	1	85	55-
1	2	75	47
1	3	81	58-
1	4	70	60-
1	5	157	133
1	6	<61	22-
1	7	<57	33-
1	8	<54	7
1	9	72	73-
1	10	49	44
1	11	<29	19
2	0	325	284
2	1	196	151
2	2	<63	52-
2	3	<63	6-
2	4	253	234-
2	5	167	137-
2	6	59	60
2	7	55	40-
2	8	193	204
2	9	169	183
2	10	81	68-
3	0	43	1
3	1	161	142-
3	2	61	58-
3	3	143	122-
3	4	138	136
3	5	120	115
3	6	96	103-
3	7	73	76
3	8	<36	5
3	9	75	80-
3	10	<24	12
4	0	385	367
4	1	173	155-
4	2	69	49-
4	3	134	106-
4	4	292	322-
4	5	183	191
4	6	75	83
4	7	73	68
4	8	271	254
4	9	158	158-
5	0	214	230-
5	1	<40	61-
5	2	<39	44
5	3	<39	29
5	4	135	129
5	5	<35	15-
5	6	<31	12
5	7	<26	37
5	8	99	131-
$\ell = 7$			
0	1	446	396-
0	3	398	347-
0	5	448	429
0	7	215	192
0	9	316	303-
1	0	<60	12-
1	1	<60	51-
1	2	<59	9-
1	3	75	69
1	4	100	89
1	5	130	132-
1	6	80	88-
1	7	<44	43
1	8	<36	30-
1	9	<24	35
2	0	355	357-
2	1	142	131-
2	2	<55	8
2	3	143	142-
2	4	356	372
2	5	135	137
2	6	92	98-
2	7	73	74
2	8	245	239-
3	0	<43	28-
3	1	73	69
3	2	45	18
3	3	54	33
3	4	69	55-
3	5	<36	48-
3	6	<33	41
3	7	<26	31-
4	0	119	114-
4	1	60	43
4	2	<41	12-
4	3	<76	81
4	4	124	111
4	5	118	101-
4	6	<29	4
5	0	74	65
5	1	<29	21-
5	2	<29	16
5	3	<26	19
5	4	75	58-
$\ell = 8$			
0	0	102	88
0	2	<43	1
0	4	<37	24-
1	0	69	43-
1	1	124	104-
1	2	<43	16-
1	3	76	63-
1	4	85	77
1	5	51	43
2	0	232	228-
2	1	125	120-
2	2	<40	6
2	3	84	85-
2	4	185	194
2	5	49	51
3	0	98	128-
3	1	<26	1
3	2	<24	53
3	3	<22	13-

shift correction was 0·0036 Å for a sulfur parameter and 0·0098 Å for a nitrogen parameter. Both of these values are approximately equal to the final calculated standard deviations of the parameters. The resulting Fourier parameters are listed in Table 1. The Fourier and least-squares parameters agree very well: the average differences are 0·001 Å and 0·005 Å for sulfur and nitrogen parameters, respectively, and the corresponding maximum differences are 0·005 Å and 0·009 Å.

A comparison of the observed and calculated Fourier peak heights is given in Table 3.

A careful search was made for the hydrogen atoms in both the observed and difference syntheses. Several peaks of proper height were found to lie within 0·5–1·5 Å from the nitrogen atoms, and one of these was 0·9 Å from N_2, along a presumed weak N–H · · · N hydrogen bond. However, since obviously spurious peaks of equal heights were also observed, it cannot be said with certainty that this peak is actually due to a hydrogen atom. It is not surprising that an unequivocal indication of the hydrogen atoms was not achieved in this crystal, since it contains relatively heavy sulfur atoms.

The final positional parameters, which are the averages of those obtained in the least squares and Fourier methods, are given in Table 1. The average difference between the final parameters and the trial parameters obtained from the Patterson function is only 0·07 Å, a result which shows that the detailed consideration of the Patterson function was quite worth while.

The final set of observed and calculated structure factors is listed in Table 4. The calculated values do not include scattering due to the hydrogen atoms. On the basis of observed planes only, the R value is 11·8 %. This value could undoubtedly (and conventionally) be reduced by omitting planes suspected of extinction, and by including the hydrogen scattering.

The calculated standard errors (Shoemaker *et al.*, 1950) in the least-squares parameters are listed in Table 1. The average standard error of a sulfur-atom parameter is 0·003 Å and the average standard error of a nitrogen-atom parameter is 0·012 Å. The corresponding standard error in a sulfur–nitrogen interatomic bond distance is 0·012 Å.

Discussion of the structure

The $S_4N_4H_4$ *molecule*

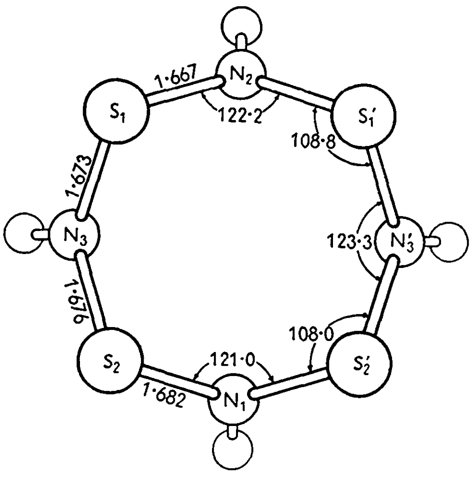

Fig. 2. The $S_4N_4H_4$ molecule.

Table 5. *Intramolecular distances and angles*

Distances		Angles	
N_1–S_2	1·682 Å	S_1–N_2–S_1'	122·2°
S_2–N_3	1·676	S_1–N_3–S_2	123·3
N_3–S_1	1·673	S_2–N_1–S_2'	121·0
S_1–N_2	1·667	N_2–S_1–N_3	108·8
		N_1–S_2–N_3	108·0
$S_1 \cdots S_1'$	2·918		
$S_2 \cdots S_2'$	2·928	S_1–S_2–S_2'	89·9
$S_1 \cdots S_2$	2·947	S_1–S_1'–S_2	90·1
$N_1 \cdots N_3$	2·716	N_1–N_3–N_2	89·9
$N_3 \cdots N_2$	2·715	N_3–N_1–N_3	90·1
		N_3–N_2–N_3	90·1

The dimensions of the $S_4N_4H_4$ molecule, as it exists in the crystal, are shown in Fig. 2. The intramolecular bond lengths and bond angles are given in Table 5. The average length of the four crystallographically independent S–N chemical bonds is 1·674 Å, the average deviation from this value being 0·004 Å. The internal consistency of the bond lengths thus leads to a much smaller standard error in the S–N bond length than that estimated from the errors in the least-squares positional parameters. The various S–N–S and N–S–N bond angles are also not significantly different, their averages being 122·2° and 108·4° respectively. The four sulfur atoms in the molecule form a square having an edge of average length 2·927 Å, and the four nitrogen atoms lie on a square having an edge of average length 2·715 Å. The four sulfur atoms must lie in a plane imposed by the mirror plane across the molecule. The equation of this plane, referred to molecule M in Fig. 3, is $0{\cdot}4099x+0{\cdot}1101z = 1$. The nitrogen atoms need not lie in a plane imposed by the

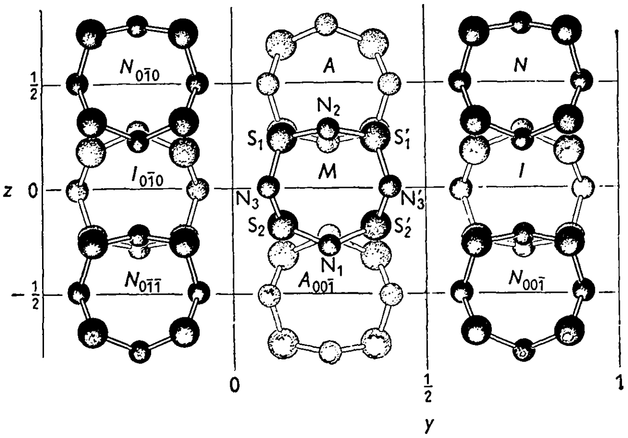

Fig. 3. The structure viewed along the *a* axis.

space group. The best least-squares plane through these atoms has the equation $0{\cdot}5597x+0{\cdot}0005y+0{\cdot}1458z = 1$, and no nitrogen atom lies farther than 0·019 Å from this plane. The two planes are parallel to within 0·5°, and the distance between them is 0·627 Å. The molecule has the symmetry $4mm$ in the crystal, but only one mirror plane is required by the space group.

The shape of the $S_4N_4H_4$ molecule is quite different from that of S_4N_4. The configuration of the S_4N_4 molecule is that of a cage (Lu & Donohue, 1944; Clark, 1952), whereas the configuration of the $S_4N_4H_4$ molecule is a regular puckered ring. This result is contrary to the view expressed by Lippincott & Tobin (1953), who concluded that the two molecules are analogous in structure, except that in $S_4N_4H_4$, two N–N bonds of S_4N_4 are broken to form four N–H bonds. The $S_4N_4H_4$ molecule is, in fact, strikingly similar to an S_8 molecule in which alternate sulfur atoms are replaced by NH groups. The sulfur bond angles in $S_4N_4H_4$ and S_8 are not significantly different, being 108·4° and 107·8° (Abrahams, 1955), respectively. Also, the dihedral angles in the two compounds are equal, the observed values for $S_4N_4H_4$ and S_8 being 99·4° and 99·3°. These structural similarities suggest that the bonding role of the sulfur atoms in $S_4N_4H_4$ is very much like that of the sulfur atoms in the S_8 molecule.

The observed S–N bond distance of 1·674 Å in $S_4N_4H_4$ is longer than the value of 1·62 Å observed by Lu & Donohue (1944) in S_4N_4, and both of these distances are shorter than the value 1·73 Å predicted for a single bond (Schomaker & Stevenson, 1941). A review by Trueblood & Mayer (1956) of S–N bond distances in various molecules shows that in almost every case the S–N bond distances observed are also shorter than that predicted for a single bond; for example: $O_2S(NH_2)_2$, 1·60 Å; KO_3SNH_2, 1·57 Å; $K_2(O_3S)_2NH$, 1·66 Å; and $KO_3SN_2O_2$, 1·63 Å. A possible explanation of these shortenings is the use of the energetically available sulfur d orbitals by the unshared pair of electrons of the nitrogen atoms. This explanation is substantiated by the lack of basic character of the nitrogen atoms of $S_4N_4H_4$, as pointed out in the introduction. The value of the S–N–S angle is of interest here, since it suggests that the σ-bonding orbitals of the nitrogen are almost pure sp^2 in character, thus leaving the nitrogen electrons in the p orbital perpendicular to the bonding plane free for π bonding. The bond angle in S_8 has been discussed in a recent review by Abrahams (1956): he stated that the observed angle of 107·8° is the angle expected between orbitals having 80% p character and 20% s character, but also presented a second interpretation that the bonding orbitals are nearly pure p in character and the angle is increased from 90° by a pivoting of the p orbitals. If one assumes that the same sulfur orbitals are used in $S_4N_4H_4$, the sulfur p orbitals, containing a non-bonding pair of electrons, will be at angle of about 90° from the p electrons of the nitrogen atom, as indicated by the value of the dihedral angle. This configuration allows almost ideal overlap of the available sulfur d orbital with the nitrogen p electron cloud, and qualitatively accounts for the observed partial double-bond character of the S–N bond. Although the above discussion is not unreasonable, the alternate possibility exists that the observed molecular conformation of $S_4N_4H_4$ is a consequence of the same $p\pi$ repulsion which Pauling (1949) invoked to explain the stability of the S_8 molecule, especially since the dihedral angles are equal in both molecules.

The value of the nitrogen bond angle strongly suggests the presence of trigonal bonding about the nitrogen atom with coplanar S–NH–S groupings. This configuration is also consistent with the molecular packing to be discussed in a later section.

Ellipsoid of thermal vibration

During the course of this work, the SWAC was programmed to solve the general temperature-factor equations in terms of a Gaussian ellipsoid of vibration (Sparks, 1957). The values obtained are the direction cosines of the principal axes of the vibration ellipsoids and the root-mean-square amplitudes of vibration along those axes. These values are listed in Table 6.

Table 6. *Principal-axis parameters of the atomic vibration ellipsoids*

Atom	i	$(\overline{r_i^2})^{\frac{1}{2}}$	q_{ia}	q_{ib}	q_{ic}
S_1	1	0·255 Å	0·98679	−0·08577	0·13743
	2	0·215	0·02318	0·91439	0·40417
	3	0·148	−0·16033	−0·39565	0·90430
S_2	1	0·209	0·83231	0·53330	−0·15118
	2	0·194	−0·54164	0·72444	−0·42639
	3	0·149	−0·11788	0·43677	0·89182
N_1	1	0·188	0·99027	0·00000	0·13917
	2	0·230	0·00000	1·00000	0·00000
	3	0·121	−0·13917	0·00000	0·99027
N_2	1	0·269	0·99954	0·00000	−0·03025
	2	0·217	0·00000	1·00000	0·00000
	3	0·115	0·03025	0·00000	0·99954
N_3	1	0·231	0·94510	0·31826	0 07412
	2	0·204	−0·32391	0·94237	0·08374
	3	0·158	−0·04320	−0·10315	0·99373

The root-mean-square amplitude of vibration along the ith axis is given as $(\overline{r_i^2})^{\frac{1}{2}}$. The values q_{ia}, q_{ib} and q_{ic} in Table 6 are the direction cosines of the ith axis with respect to the three crystallographic axes. The values of $(\overline{r_i^2})^{\frac{1}{2}}$ are roughly comparable for all of the atoms, and are reasonable for a molecular crystal. The most interesting feature of these parameters is that the least amount of vibration of all of the atoms is roughly parallel to c, indicating stronger intermolecular attraction in this direction. This is in fact true, and it will be shown in the next section that the only hydrogen bonding in the crystal is in this direction.

Molecular environment

In Figs. 3, 4 and 5 are given, respectively, views of the structure looking along the a axis in the direction of decreasing x, along the b axis only at those molecules lying across the mirror plane at $y = \frac{1}{4}$, and along the c axis in the direction of increasing z. The origin of the cell is the same in every drawing and the system of axes is right-handed.

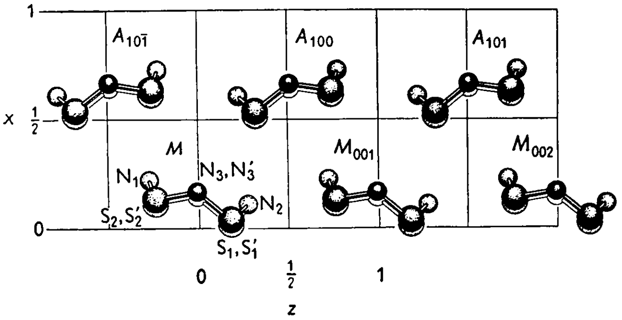

Fig. 4. The structure viewed along the b axis. Atoms related by the plane of symmetry perpendicular to b have been displaced slightly to show the molecules more clearly.

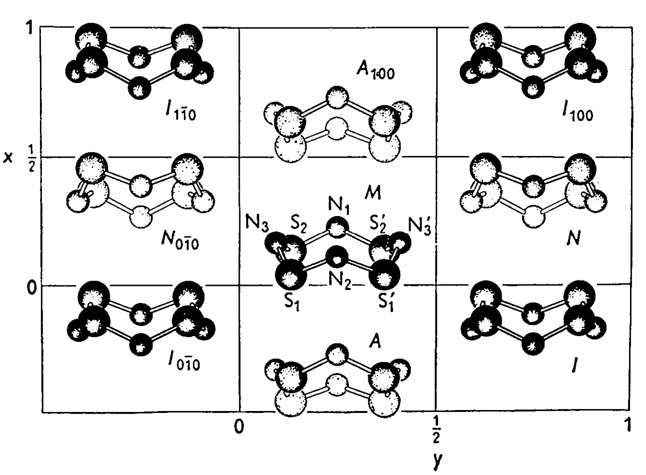

Fig. 5. The structure viewed along the c axis.

In all three drawings the environment is discussed in detail around the molecule designated by M, with the atomic coordinates (x, y, z) found in Table 1. Three other molecules related to M by an a glide perpendicular to c, an n glide perpendicular to a, and a center of symmetry are designated, respectively, A, M and I. All other molecules shown are related to these four by lattice translations and are designated by the same letters but with subscripts denoting the lattice translation vector; M_{qrs}, for example, is related to molecule M by the vector $qa+rb+sc$. The hydrogen atoms are not shown in these diagrams, since their positions were determined largely on the basis of the discussion which follows.

The intermolecular contacts involving the unique atoms of molecule M are summarized in Table 7. The list is somewhat redundant in that a few symmetrically equivalent contacts are listed twice in order to give a complete listing of each atomic environment.

Table 7. *Intermolecular distances*

From atom x in molecule M	to atom y	in molecule	Distance, xy
N_2	N_1	M_{001}	3·160 Å
N_2	S_2	M_{001}	3·628
N_2	S_1	A_{100}	3·815
N_1	S_1	$A_{10\bar{1}}$	3·742
N_1	S_2	$A_{10\bar{1}}$	3·561
N_1	S_1'	$A_{10\bar{1}}$	3·742
N_1	S_2'	$A_{10\bar{1}}$	3·561
N_3	S_2'	$N_{0\bar{1}0}$	3·603
N_3	S_2	$I_{0\bar{1}0}$	4·015
N_3	N_3	$I_{0\bar{1}0}$	3·510
N_3	S_1	$I_{0\bar{1}0}$	3·400
N_3	S_1'	$N_{0\bar{1}\bar{1}}$	3·745
N_3	S_2	$A_{10\bar{1}}$	4·150
N_3	S_1	A_{100}	3·735
S_1	S_1	A_{100}	4·110
S_1	S_2	M_{001}	4·027
S_1	N_2	A	3·815
S_1	S_2'	$N_{0\bar{1}0}$	4·139
S_1	S_2	$I_{0\bar{1}0}$	3·509
S_1	N_3	$I_{0\bar{1}0}$	3·400
S_1	N_3	A	3·735
S_2	S_2	$A_{00\bar{1}}$	4·005
S_2	N_1	$A_{00\bar{1}}$	3·561
S_2	S_1	$N_{0\bar{1}\bar{1}}$	4·139
S_2	S_1	$I_{0\bar{1}0}$	3·509
S_2	N_3	$A_{00\bar{1}}$	4·150

The shortest observed intermolecular distance is 3·160 Å between atom N_2 of molecule M and atom N_1 of molecule M_{001}. This distance is comparable to a normal van der Waals contact, such as the N–N contact of 3·15 Å in dicyandiamide (Hughes, 1940). However, if one considers this contact to be an N_2–H $\cdots$ N_1 hydrogen bond, both the $N_2 \cdots N_1$ distance and the S_1–$N_2 \cdots N_1$ angle of 116·6° agree well with previous values reported in the literature (Donohue, 1952). A hydrogen bond in this direction is compatible with the molecular configuration postulated above wherein the nitrogen atoms are trigonally bonded, and also explains the smaller amount of thermal motion observed in the direction of the c axis.

If the other nitrogen atoms are similarly bonded, then their environments in the crystal should show vacancies in which to place their bonded hydrogen atoms. It can be seen clearly in Fig. 4 that N_1 is roughly equidistant from the square of sulfur atoms of molecule $A_{10\bar{1}}$, and reference to Table 7 shows that these distances are considerably longer than the van der Waals contact of 3·3 Å. There is, however, sufficient room for a hydrogen atom, trigonally bonded to the nitrogen atom, to be placed within the cavity between this sulfur square of $A_{10\bar{1}}$ and N_1 of molecule M. In fact, if one assumes that the hydrogen atom is 1·01 Å from N_1 at an S_2–N_1–H angle equal to the angle of the S_1–$N_2 \cdots N_1$ hydrogen bond angle, then the four H $\cdots$ S contacts are between 3·0 and 3·1 Å, values which agree very satisfactorily with the accepted van der Waals contact. The N_3 atoms in the crystal lie very nearly in planes perpendicular to the c axis at $z = 0$ and $z = \frac{1}{2}$. Above and below these nitrogen atoms are roughly planar layers of sulfur atoms centered at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. This configuration results in a cage of sulfur atoms surrounding the N_3 atom, as shown in Fig. 4. The various $N_3 \cdots S$ distances (Table 7) range from 3·400 Å, which is slightly larger than a van der Waals contact, up to 4·150 Å. There is also an $N_3 \cdots N_3'$ distance of 3·510 Å across the center of symmetry. Since the molecules are touching in the z direction through N_2–$H \cdots N_1$ hydrogen bonds, and in the x direction through N_1–$H \cdots S$ contacts, the really important contacts of atom N_3 of molecule M will be those in the y direction with molecules $I_{0\bar{1}0}$, $N_{0\bar{1}0}$ and $N_{0\bar{1}\bar{1}}$. The sulfur atoms S_1 and S_2 of molecule M are, respectively, in van der Waals contact with atoms S_2 and S_1 of molecule $I_{0\bar{1}0}$. The contacts of atom N_3 of M with atoms S_1 and N_3 of $I_{0\bar{1}0}$ are thus about what one would expect. Atom N_3 of molecule M is 3·603 Å from atom S_2' of molecule $N_{0\bar{1}0}$ and 3·745 Å from atom S_1' of molecule $N_{0\bar{1}\bar{1}}$. These distances are considerably longer than van der Waals contacts, but if one assumes an N_3–H bond similar to the assumed N_1–H and N_2–H bonds, the resulting hydrogen atom will be about 3·0 Å from atom S_2' of molecule $N_{0\bar{1}0}$ and at a slightly greater distance from atoms N_3 and S_2 of molecule $I_{0\bar{1}0}$.

There are, on the other hand, no holes in the structure which would allow placement of the hydrogen atoms in positions corresponding to S–H rather than N–H bonds. The molecular packing of $S_4N_4H_4$ is thus readily explained and internally consistent with the assumption that the hydrogen atoms are chemically bonded to nitrogen. Moreover, the three perturbed N–H streching frequencies observed by Lippincott & Tobin are also in agreement with the three types of environment around atoms N_1, N_2 and N_3. This evidence, plus that obtained from a consideration of the isolated molecule and the thermal vibration parameters, leaves no doubt that $S_4N_4H_4$ contains N–H bonds with nearly coplanar S–NH–S groupings.

(*Added in proof*).—In a short paper in a recent number of Acta Chemica Scandinavica which arrived in our library after the present paper had been accepted for publication, Lund and Svendsen (1957) describe briefly the results of their X-ray study of $S_4N_4H_4$. Our results are in substantial agreement with theirs: both studies found the same unit cell-dimensions (within ±0.15%) and space group. Lund and Svendsen used 107 reflections in two prism zones, and their sulfur and nitrogen parameters differ from ours by an average of 0.008 Å and 0.023 Å respectively. They made no attempt to locate the hydrogen atoms, either directly or indirectly, nor did they take account of thermal anisotropy. Since our study used nearly complete data accessible to Cu$K\alpha$, a more detailed comparison seems out of place, but it is gratifying that the two methods used led to very nearly the same results.

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