Chemistry. — *The Crystalstructure of Nitrogen-tetrasulphide and Tetra-hydro-nitrogentetrasulphide.* By F. M. JAEGER and J. E. ZANSTRA.

§ 1. *Nitrogen-tetrasulphide:* N_4S_4 was discovered by SOUBEIRAN [1]), and later-on studied by different authors [2]). SCHENCK [3]) determined its molecular weight as corresponding to the formula : N_4S_4 ; BERTHELOT and VIEILLE [4]) measured its heat of decomposition. It is a crystalline substance, which is a strongly *endothermic* compound and accordingly highly explosive; its production is accompanied by a considerable negative heat-effect : $Q = - 128000$ calories per gramme-molecule. It can be prepared in several ways, for instance by the interaction of SCl_2 or $SOCl_2$ and NH_3. In the pure state the colour of the crystalline substance is pale yellow or orange-yellow; it can be recrystallised from several organic solvents. It readily volatilizes at 135° C. and, according to SCHENCK, melts at 178° C.

The *nitrogen-tetrasulphide* was dissolved in benzene; on slow evaporation at room-temperature, small orange-yellow and very brilliant crystals were obtained, showing the forms pictured in the figure 1.
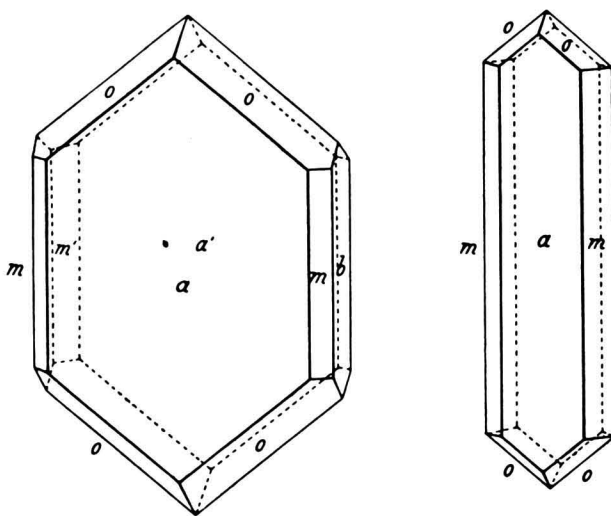

Fig. 1. Nitrogen - tetrasulphide.

[1]) E. SOUBEIRAN, Ann. de Chim. et Phys., (2), **67**, (1838), 71, 96.

[2]) A review of the literature is given in the paper of O. RUFF and E. GEISEL, Ber. d. d. chem. Ges., **37**, (1904), 1575.

[3]) R. SCHENCK, Ann. der Chemie, **290**, (1896), 176.

[4]) M. BERTHELOT and P. VIEILLE, Comp. rend. Paris, **96**, (1883), 214.

Rhombic-bipyramidal [1]).

The axial ratio was determined at : $a : b : c = 1.039 : 1 : 0.842$, — values which are in good agreement with those calculated from the results of the X-ray-examination : $a : b : c = 1.0472 : 1 : 0.8512$.

Forms observed : $a = \{100\}$, predominant, larger than $b = \{010\}$, which is often absent ; $m = \{110\}$, yielding good reflections ; $o = \{111\}$, small, but easily measurable. The shape of the crystals is elongated parallel to the c-axis and tabular parallel to $\{100\}$.

Angular values:	*Observed:*		*Calculated:*	
$a : m = (100) : (110) =^*$	$46°$	$6'$	—	
$o : o = (111) : (\bar{1}11) =^*$	63	36	—	
$b : m = (010) : (110) =$	43	50	$43°$	$54'$
$m : m = (110) : (\bar{1}10) =$	88	0	87	48
$a : o = (100) : (111) =$	58	20	58	$12\frac{1}{2}$
$o : o = (111) : (1\bar{1}1) =$	66	30	66	23
$b : o = (010) : (111) =$	56	42	56	$48\frac{1}{2}$
$m : o = (110) : (111) =$	40	30	40	33

No distinct cleavability was observed.

On $\{100\}$, $\{010\}$ and $\{110\}$ a rectangular extinction occurs. The crystals are dichroïtic : on $\{100\}$ and $\{110\}$: yellow, for vibrations parallel to the c-axis ; orange, for those perpendicular to this direction. The plane of the optical axes seems to be parallel to $\{001\}$; evidently the apparent angle of the optical axes is only small.

The specific gravity of the crystals at 18° C. was determined at : 2.23.

§ 2. In the first place a number of powder-spectrograms were prepared after HULL-DEBIJE's method, copper-a- and β-radiation being used at a tension of 50000 Volts. The results are tabulated in Tables I and II ; the data in Table II are the mean values of the measurements of *five* different spectrograms. They showed a great number of lines : in using a camera of 57.2 mm. radius, no less than 144 lines were present on the photographs obtained.

Evidently we have to deal here with a structure derived from the simple orthorhombic lattice, the elementary cell of which contains : 16 sulphur-, and 16 nitrogen-atoms. Its parameters approximately are : $a_0 = 8.76$ Å ; $b_0 = 8.44$ Å ; and $c_0 = 7.11$ Å.

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[1]) We never found any indication of a monoclinic symmetry, as NICKLÈS, Ann. de Chim. et Phys., (3), **32**, (1851), 420, suggested.

| | TABLE I. |
| | Powder-Spectogram of Nitrogen-tetrasulphide: $N_4 S_4$. |

No. of Line:	$2l$ in m.M.:	Estim. Intens.:	Wave-length λ:	Angle Θ:	$Sin^2 \Theta$ (observed):	$Sin^2 \Theta$ (calculated):	Indices (hkl):
1	22.0	2	α	5° 25′	0.0089	0.0083	(010)
2	27.0	5	α	6 46	0.0139	0.0117	(001)
3	29.0	5+	α	7 15	0.0159	0.0160	(110)
4	33.7	3	$\alpha (\beta)$	8 26	0.0215	0.0200 or 0.0194 or 0.0226	(011) . (101) . (111)
5	38.0	10	α	9 34	0.0276	0.0277	(111)
6	40.6	9	α	10 10	0.0312	0.0308	(200)
7	42.9	3+	$\alpha (\beta)$	10 45	0.0348	0.0332 or β : 0.0345	(020) ; β : (201)
8	48.1	5−	α	12 3	0.0436	0.0425	(201)
9	50.6	1	β	12 39	0.0489	0.0511	(112)
10	52.0	3	α	13 1	0.0507	0.0508	(211)
11	58.3	6	α	14 36	0.0635	0.0628	(112)
12	59.1	2	$\alpha (\beta)$	14 48	0.0652	0.0640 or 0.0632	(220) . (202) . (310)
13	62.1	2−	α	15 50	0.0735	0.0694 or 0.0747	(300) . (030)
14	64.8	10	α	16 13	0.0780	0.0776 or 0.0777	(202) . (310)
15	68.6	4	α	17 11	0.0873	0.0876	(122)
16	72.6	1	α	18 11	0.0974	0.0940 or 0.1024	(131) . (320)
17	75.9	3	α	19 0	0.1060	0.1055	(230)
18	77.9	3−	α	19 30	0.1114	0.1107	(222)
19	79.4	5−	α	19 53	0.1157	0.1142 or 0.1161	(321) . (302)
20	80.5	5	α	20 9	0.1187	0.1214 or 0.1171 or 0.1212	(032) . (231) . (113)
21	82.1	3+	α	20 33	0.1232	0.1244 or 0.1233	(312) . (400)
22	83.8	3	α	20 59	0.1282	0.1291	(132)
23	87.2	4	α	21 49	0.1381	0.1360 or 0.1384	(203) . (023)
24	90.0	4	α	22 32	0.1468	0.1432 ; 0.1461 or 0.1441	(411) . (123) . (213) . (330)
25	92.6	5	α	23 11	0.1550	0.1557 or 0.1564	(331) . (420)
26	95.0	4	α	23 48	0.1628	0.1635	(240)
27	96.8	4	α	24 14	0.1685	0.1692 or 0.1700	(223) . (402)
28	100.1	5	α	25 4	0.1795	0.1799	(033)
29	101.6	4	α	25 26	0.1844	0.1828	(313)
30	104.8	2	α	26 14	0.1954	0.1876 or 0.1909	(133) . (332) . (014)
31	106.8	2	α	26 44	0.2024	0.2030	(114)
32	108.8	2	α	27 15	0.2098	0.2074 or 0.2077	(050) . (323)
33	111.7	2	α	27 58	0.2199	0.2191	(051)
34	115.4	2	α	28 54	0.2335	0.2280	(124)
35	117.2	1	α	29 17	0.2393	0.2376 or 0.2382	(413) . (250)
36	119.5	2	α	29 55	0.2487	0.2456 or 0.2488 or 0.2499	(143) . (342) . (251) . (512)
37	121.6	2	α	30 27	0.2568	0.2559	(440)
38	122.8	2	α	30 45	0.2614	0.2616 or 0.2619	(423) . (152)
39	123.9	3	α	31 1	0.2655	0.2672 or 0.2688	(530) . (243)

No. of Line:	2l in m.M.:	Estim. Intens.:	Wave-length λ:	Angle Θ:		Sin² Θ (observed):	Sin² Θ (calculated):	Indices (hkl):

TABLE I (Continued).
Powder-Spectogram of Nitrogen-tetrasulphide: $N_4 S_4$.

No. of Line:	2l in m.M.:	Estim. Intens.:	Wave-length λ:	Angle Θ:	Sin² Θ (observed):	Sin² Θ (calculated):	Indices (hkl):
40	125.2	2	α	31° 21′	0.2707	0.2725	(522)
41	126.7	2	α	31 44	0.2768	0.2772	(600)
42	130.9	1	α	32 47	0.2932	0.2925	(234)
43	133.3	4	α	33 23	0.3028	0.3027	(442)
44	137.2	1	α	34 21	0.3184	0.3181 or 0.3198	(161) . (044)
45	139.6	2	α	34 57	0.3284	0.3275 or 0.3309	(144) . (523)
46	142.2	2	α	35 37	0.3391	0.3369 or 0.3411	(541) . (261)
47	143.5	2	α	35 56	0.3444	0.3423 or 0.3435	(451) . (253) . (424)
48	144.2	2	α	36 37	0.3474	0.3506	(244)
49	146.4	2	α	36 40	0.3563	0.3563 or 0.3572	(225) . (622)
50	148.5	2	α	37 11	0.3653	0.3636 or 0.3669	(631) . (035)
51	150.7	2	α	37 44	0.3745	0.3720 ; 0.3746 ; 0.3762 ; 0.3773	(542) . (533) . (135) . (262) . (700)
52	155.3	2	α	38 51	0.3935	0.3944 or 0.3948	(054) . (325)
53	157.8	2	α	39 31	0.4049	0.4021 ; 0.4039 or 0.4065	(154) . (063) . (070)
54	160.8	1	α	40 16	0.4178	0.4155	(623) . (170) . (071)
55	163.2	1	α	40 50	0.4275	0.4286 or 0.4292	(106) . (016)
56	166.5	2	α	41 41	0.4424	0.4430	(444)
57	178.2	2	α	44 38	0.4936	0.4932 or 0.4943	(515) . (164) . (345)
58	185.0	1	α	46 19	0.5230	0.5234	(326)
59	189.6	2	α	47 29	0.5433	0.5441	(406)
60	194.4	1	α	48 41	0.5641	0.5613 or 0.5690	(146) . (355)
61	201.5	2	α	50 28	0.5948	0.5969	(644)
62	204.7	1	α	51 16	0.6085	0.6089	(464)
63	209.2	1	α	52 23	0.6275	0.6283	(056)
64	213.5	2	α	53 28	0.6456	0.6466	(526)
65	215.9	2	α	54 19	0.6598	0.6591	(256)
66	220.0	1	α	55 5	0.6724	0.6717	(654)
67	225.0	1	α	56 21	0.6930	0.6922	(555)
68	228.4	1	α	57 12	0.7066	0.7064	(616)
69	230.8	1	α	57 54	0.7176	0.7141	(465)
70	246.0	1	α	61 41	0.7750	0.7769	(655)
71	259.7	1	α	65 2	0.8218	0.8208	(556)
72	274.0	1	α	68 35	0.8667	0.8682	(665)

Radius of Camera: 57.2 m.M.   Exposure: 50 m. Amp hours.
Wave-Length: $\lambda_\alpha = 1.540$ Å.; $\lambda_\beta = 1.388$ Å.
Quadratic Equation:

$$sin^2 \Theta = 0.007701 . h^2 + 0.008296 . k^2 + 0.011691 . l^2 \quad \ldots \ldots \ldots (\alpha)$$

$$sin^2 \Theta = 0.006272 . h^2 + 0.006757 . k^2 + 0.009521 . l^2 \quad \ldots \ldots \ldots (\beta)$$

Parameters of the Lattice:

$$a_0 = 8.76 \text{ Å.}; \quad b_0 = 8.44 \text{ Å.}; \quad c_0 = 7.11 \text{ Å.}$$

Specific Weight: 2.23; calc.: 2.32. The elementary cell contains $N_{16} S_{16}$.
Simple orthorhombic lattice.

No. of Line:	$2l$ in m.M.:	Estim. Intens.:	Wave-length λ:	Angle Θ:		$Sin^2 \Theta$ (observed):	$Sin^2 \Theta$ (calculated):	Indices (hkl):
1	22.6	4+	α	7°	18'	0.0161	0.0160	(110)
2	26.3	1	β	8	29	0.0218	0.0200 ; 0.0225	α : (011) ; β : (111)
3	29.2	9	α	9	25	0.0268	0.0277	(111)
4	31.4	7	α	10	8	0.0309	0.0308	(200)
5	33.2	1	α	10	43	0.0346	0.0332	(020)
6	36.3	2	α	11	43	0.0412	0.0409 ; 0.0425	(120) . (201)
7	39.5	1	α	12	44	0.0486	0.0511	(112)
8	40.6	2	β	13	6	0.0514	0.0509	(211)
9	44.6	6	α	14	23	0.0617	0.0628	(112)
10	45.6	5	α	14	43	0.0645	0.0640	(220)
11	49.7 ⟩	10 ⟩	α	16	2 ⟩	0.0763 ⟩	0.0766	⟩ (030) . (202) or (310)
12	50.5 ⟨	10 ⟨	α	16	17 ⟩	0.0786 ⟩	0.0766	⟩
13	52.9	2	α	17	4	0.0861	0.0876	(122)
14	55.8	1	α	18	0	0.0955	0.0940	(131)
15	59.7	2	α	19	16	0.1089	0.1055	(230)
16	62.7	3+	α	20	13	0.1194	0.1171	(231) . (400)
17	66.7	3	α	21	31	0.1345	0.1349 ; 0.1360	(401) . (203)
18	69.9	3	α	22	33	0.1471	0.1461 ; 0.1492	(123) . (322)
19	73.3	7	α	23	39	0.1609	0.1635	(240)
20	75.7	2	α	24	25	0.1709	0.1692 ; 0.1701	(223) . (402)
21	78.3	2	α	25	16	0.1822	0.1828	(313)
22	80.0	1	α	25	49	0.1897	0.1876 ; 0.1907	(133) . (332)
23	82.5	2	α	26	37	0.2007	0.2008 ; 0.2030	(510) . (114)
24	85.8	2	α	27	41	0.2158	0.2151	(150)
25	90.6	2	α	29	14	0.2385	0.2382 ; 0.2392	(250) . (502)
26	93.8	2	α	30	16	0.2540	0.2542 ; 0.2559	(052) . (440)
27	96.0	3	α	30	58	0.2647	0.2672	(530)
28	98.6	2	α	31	49	0.2779	0.2772	(600)

TABLE II.

Five Powder-Spectograms of Nitrogen-tetrasulphide N_4S_4.

TABLE II (*Continued*).

Five Powder-Spectrograms of Nitrogen-tetrasulphide N_4S_4.

No. of Line:	$2l$ in m.M.:	Estim. Intens.:	Wave-length λ:	Angle Θ:	$Sin^2\Theta$ (observed):	$Sin^2\Theta$ (calculated):	Indices (hkl):
29	100.8	3	α	32° 32′	0.2892	0.2884 ; 0.2889 or 0.2895	(351).(601).(324)
30	103.8	3	α	33 29	0.3044	0.3031 ; 0.3064	(433).(513).(160)
31	107.8	2	α	34 49	0.3260	0.3253 ; 0.3254 or 0.3275	(352).(052).(144)
32	111.7	1	α	36 2	0.3460	0.3454	(062)
33	114.4	2	α	36 55	0.3608	0.3612 ; 0.3616	(443).(305)
34	117.7	1	α	37 59	0.3788	0.3773 ; 0.3796	(700).(452).(504).(361)
35	124.1	2	α	40 2	0.4138	0 4128 ; 0.4147 or 0.4155	(524).(362).(170).(405)
36	128.8	1	α	41 33	0.4399	0.4369	(116)
37	132.0	1	α	42 35	0.4579	0.4571 ; 0.4567	(633).(642)
38	138.1	2	α	44 33	0.4922	0.4931 ; 0.4934	(515).(164)
39	143.0	1	α	46 8	0.5198	0.5177 ; 0.5180	(454).(525)
40	146.0	1	α	47 6	0.5366	0.5379	(562)
41	150.2	1	α	48 28	0.5603	0.5613	(146)
42	172.0	1	α	55 29	0.6789	0.6782	(564)

Radius of Camera: 44.4 m.M. Exposure: 50 m. Amp. hours.

Wave-Length: $\lambda_\alpha = 1.540$ Å.; $\lambda_\beta = 1.388$ Å.

Quadratic Equation:

$$sin^2\Theta = 0.0077 . h^2 + 0.008296 . k^2 + 0.01169 . l^2. \quad\quad\quad\quad (\alpha)$$
$$sin^2\Theta = 0.00627 . h^2 + 0.006757 . k^2 + 0.00952 . l^2. \quad\quad\quad\quad (\beta)$$

Parameters of the Lattice:

$$a_0 = 8.76 \text{ Å}; \; b_0 = 8.44 \text{ Å}; \; c_0 = 7.11 \text{ Å}.$$

Specific Weight: 2.23; calc.: 2.32. The simple orthorhombic cell contains 16 S-, and 16 N-Atoms.

§ 3. A number of rotation-spectrograms were prepared, — the crystals consecutively being rotated about their a-, b- and c-axes, — with the purpose of determining the identity-distances I_a, I_b and I_c. In these experiments the α- and β-radiation from a *copper*-anticathode was used ; the spectrograms were analysed according to BERNAL's method.

The distances I_a, I_b, and I_c thus obtained were corrected by means of oscillation-spectrograms (BRAGG) on (100), (010), (111) and (110), — *calcite* being used for the purpose of comparison.

From the rotation-spectrograms, the following values were deduced :
$I_a = 8.87$ Å; $I_b = 8.47$ Å; $I_c = 7.21$ Å; a rotation-spectrogram round [110] gave: $I_{(110)} = 12.02$ Å.

The BRAGG-spectrogram on (100) gave a second order spectrum from which $d_{(100)}$ was calculated to be: 4.44 Å. On (010) a third and a fifth order spectrum were observed, giving $d_{(010)} = 8.47$ Å. In the same way on (110) a second order spectrum was found, from which $d_{(110)}$ was calculated at: 6.03 Å. The BRAGG-spectrogram on (111) gave: $d_{(111)} = 4.64$ Å, while, for a first order spectrum the calculated value would be: 4.67 Å.

From all this, the exact identity-distances appear to be :

$$I_a = 8.87 \text{ Å.}; \quad I_b = 8.47 \text{ Å} \quad \text{and} \quad I_c = 7.2 \text{ Å.}$$

As the volume of the elementary cell is, therefore, equal to 540.94 Å^3, and its weight : $1202.5.10^{-24}$ grammes, it must contain a mass equal to that of 4 molecules N_4S_4.

Hence for α-Cu-radiation, the true quadratic equation becomes :

$$sin^2\theta = 0.007536 . h^2 + 0.008265 . k^2 + 0.01140.1^2.$$

As to the question, whether the 4 molecules of N_4S_4 are, as such, really present within the elementary cell, we can remark already here, that this is highly probable indeed. *Nitrogen-tetrasulphide* has a low melting-point (178° C.) and readily sublimes (135° C.) ; these facts indicate that the linkage of the components within the lattice is not a very strong one, so that the supposition that an ionic lattice is present here, can beforehand be rejected. If the *sulphur*-atoms are represented, according to BRAGG's views, as spheres of about 2.18 Å diameter and the *nitrogen*-atoms as such of a diameter of 1.4 Å, — the total volume of these 32 spheres would be about : 109.8 Å^3, — which is only about 1/5 of the volume of the elementary cell. This fact convincingly demonstrates, that the contents of the cell cannot be closely-packed ; and it also makes it probable, that there are separate molecules present in it, which are located at rather great distances from each other.

§ 4. *Analysis of the rotation-spectrograms.*

A. *Rotation-spectrogram about* [100].

(Time of Exposure : 16 m. Amp. hours, at 40000 Volts ; angle of oscillation : (30° + 30°.) The image showed a principal spectrum and four accessory spectra. The following reflections [1]) (only for α-Cu-radiation) were observed :

Principal Spectrum : (011); *(021); *(022); (013); (041); (042); (051) or (024); (052); (005); (044); (054); (045) or (006); (064).

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[1]) The reflections indicated by * are the most intensive ones.

1st *Accessory Spectrum*: (111); (121); (112); (122); (113); (141); (142); (114); (143); (152); (160); *(162); (170) or (163); (145); (164); (173).

2nd *Accessory Spectrum*: (211); (221); (212); (231); (232); (240); (204); (250); (243); (260); (253); *(262); (235); (254); (271); (245) or (206).

3d *Accessory Spectrum*: *(310); (311); (302); *(312); *(330); *(322); *(303); (313); (340); (333); (350); (324); (352); (305); (361); (335); (354); (345) or (306); (316).

4th *Accessory Spectrum*: (411); *(420); *(421); *(412); (430); (403); (432); (441) or (423); (442) or (433); (450); (405); (462); (435); (454); (445) or (406).

B. *Rotation-Spectrogram about* [010].

Exposure and angle of oscillation as previously mentioned.

The image showed a principal and four accessory spectra.

Principal Spectrum: (200); (300); (402); (403); (304); (205); (404); (602); (504); (006); (405); (603).

1st *Accessory Spectrum*: (211); **(310) or (212); (312); (213) or (411); (412); (014) or (510); (114); (214); (015) or (513); (612); (215); (514); (415) or (711).

2nd *Accessory Spectrum*: (220); (022); (221); (222); (320); (023); (322); *(420); (223); (422); (425); (524); (424); (620); (520); (025); (522); (225); (523); (622); (623); (026); (620); (722).

3d *Accessory Spectrum*: (131); (230); (032); (231); (330); (232); *(331); *(332); (233); (431); (134); (432); (234); (530); (035); (531); (532); (334); (434); (235); (533); (534); (631); (632); (633).

4th *Accessory Spectrum*: (141); (240); (241); (042); (242); (340); (043); *(243); (342); (144); (442); *(244); (344); *(443); (541); *(542); (045); (543); (245); (444); (640); (642); (644); (742).

C. *Rotation-Spectrogram about* [001].

Exposure and oscillation-angle as indicated above.

The very beautiful photogram showed a principal spectrum and three accessory spectra.

Principal Spectrum: (110); (220); (300); *(310) or *(030); (130); (230); *(400); (040); (330); (240); (430); *(340); (150); (520); (250); (440); (530); *(600) or *(350); (160); (450) or (260); *(360); (710); (550); (720); (460) or (170); (270); (730); (650) or (370); (560); (700); (180); (830).

1st *Accessory Spectrum*: *(111); *(201); (121); *(221); (301); (311); (131); (321); (231); (401); *(041); *(331); (421); (241); (341); (151); (521); (251); (441); (531); *(601) or *(351); (611); (061); (161); (541); (451) or (261); (361); (711); (551); (721) and (641); (461) or (171); (731) or (271); (801) or (371); (561); (701); (181).

2nd *Accessory Spectrum* : *(112); *(202); *(022); (212); (122); (222); (302); (312) or (032); (132); (322); *(232); (402); (412); *(042); (332); (422); (242); (432); (052); (342); (152); (522); (252); (442); (532); (602) or (352); (612); (062); (622); (162); (542); (452); (612); (262); (632); (362); (712); (552); (722); (072); (642); (462); (172); (272); (732); (652); (372); (802); (562); (702).

3d *Accessory Spectrum* : *(113); (203); (023); (213); (123); *(313); *(033); (133); *(323); (233); (403); *(043); (333); (423); *(243); (503); (433); (343); (153); (523); (443); (533); (603) or (353); (613); (063); (163); (453); (263); (633); (363); (713); (553); (463); (173); (733); (273).

§ 5. The difficulty of determining the real structure of this substance is much greater than in the case of $H_4N_4S_4$, because, — as may be seen from the previous data, — there are almost *no* typical extinctions, but, on the contrary, all kinds of reflections appear to occur. The only certain indication is the fact, that on {100} the even order reflections are more intensive than the odd ones. Moreover, as the X-ray-spectrograms of N_4S_4 and of $H_4N_4S_4$ have not much in common, it is unfeasible directly to compare the two structures, even if the orientation of the crystals be altered by a suitable interchange of the axes a and c.

The characteristic reflections $(o\,k\,l)$, $(h\,o\,l)$ and $(h\,k\,o)$ observed, systematically arranged, are the following : (see the table on page 791).

From these reflections it follows that the structure has the symmetry of the space-group V_H^1. Its symmetry is such, that the edges of the elementary cell, the three perpendiculars in the centres of its limiting planes and the intersections of these with the planes perpendicular through each pair of the three perpendiculars just mentioned, are all binary rotatory axes ; while all the planes previously indicated are mirror-planes of the structure. Furthermore, as the diffracting power of the *sulphur*-atoms is about twice as strong as that of the *nitrogen*-atoms, it is clear, that the position of the S-atoms must first be established, because the diffraction-effects observed will, — in first instance, — be dominated by the configuration of these atoms within the elementary cell. All tentatives to fill up the cell by means of "plane rings", — as would be suggested by the usual chemical formula, — proved to be *un*successful for the explanation of the observed intensities ; and exactly the same appeared to be the case with $H_4N_4S_4$.

In the space-group V_H^1 eight one-fold places are possible ; the other 8 S-atoms would then have to be distributed over less symmetrical positions. As the S-atoms have about the same function in the structure, it is highly improbable that such an arrangement would really occur. As the group V_H^1 does not possess any sixteen-fold positions, neither the 4 S-atoms of the same molecule, nor all 4 molecules within the cell can, from the structural point of view, be quite identical. Therefore, the 4 S-atoms in the molecule

I. $a = 0.$						
(010)	(020)	(030)	(040)	*(050)	(060)	(070)
(011)	*(021)	*(031)	(041)	(051)	(061)	(071)
(012)	*(022)	(032)	*(042)	(052)	(062)	(072)
(013)	*(023)	*(033)	*(043)	(053)	(063)	
(014)	(024)	*(034)	(044)	(054)	(064)	
(015)	(025)	(035)	(045)			
(016)	(026)					
$k=1$	$k=2$	$k=3$	$k=4$	$k=5$	$k=6$	$k=7$

II. $b = 0.$						
(001)	(002)	*(003)	*(004)	(005)	(006)	(007)
*(101)	(102)	*(103)	*(104)	(105)	(106)	
(201)	*(202)	*(203)	(204)	(205)	(206)	
*(301)	*(302)	*(303)	(304)	(305)	(306)	
(401)	(402)	(403)	(404)	(405)	(406)	
(501)	*(502)	(503)	(504)			
*(601)	(602)	(603)				
(701)	(702)	(703)				
(801)	(802)					
$l=1$	$l=2$	$l=3$	$l=4$	$l=5$	$l=6$	$l=7$

III. $c = 0.$						
*(100)	*(200)	(300)	*(400)	(500)	(600)	(700)
(110)	*(210)	*(310)	(410)	*(510)	*(610)	(710)
*(120)	*(220)	(320)	*(420)	(520)	*(620)	(720)
(130)	(230)	*(330)	(430)	(530)	*(630)	(730)
(140)	(240)	(340)	(440)	*(540)	(640)	
(150)	(250)	(350)	(450)	(550)	(650)	
(160)	(260)	*(360)	(460)	(560)		
(170)	(270)	(370)				
$h=1$	$h=2$	$h=3$	$h=4$	$h=5$	$h=6$	$h=7$

are either not identically placed, or the orientation of the 4 molecules within the cell is not identical ; it is also possible, that both conditions are simultaneously fulfilled.

On the faces {100} and {010} the first order reflections are rather weak ; but this is not the case on the face {001}, although its reflections in general show only feeble intensities. The {001}-planes of the structure seem to be only loosely packed, but in the direction of the c-axis there seem to be many parameters. This can be expected, if the c-axis has the direction of a binary symmetry-axis of each molecule N_4S_4. As the even order reflections on {100} are strong, we can suppose that the planes {100} also contain atoms, which have no parameters with respect to the a-axis : (020) is weak, (220) and (420) are strong, (620) is weak ; (002) is weak, (202) is strong, (402) is weak ; etc.

It is worth remarking that the reflections (030) and (050) on the b-axis are strong, but (040) is only feeble. This can be explained, if atoms are present in the direction of the b-axis which are shifted with respect to each other over about $0.33 \cdot I_b$. Although the distances I_a and I_b appear to be rather analogous in size, the arrangement of the atoms along these two axes must, however, be different, as follows from the intensities of the reflections on the {100}- and {010}-planes.

Although two- and eight-fold positions cannot be excluded when attributing a suitable place to the atoms within the cell, — we have preferred the *fourfold* positions, — in analogy to what seems to occur in the case of $H_4N_4S_4$, where there is much more certainty about the real positions of the atoms.

The parameters u, v, w of these places have the general symbols [1]) :

1. $0\, v_1 w_1$; $0\, \bar{v}_1 w_1$; $0\, v_1 \bar{w}_1$; $0\, \bar{v}_1\, \bar{w}_1$.   3. $\tfrac{1}{2}\, v_3 w_3$; $\tfrac{1}{2}\, \bar{v}_3 w_3$; $\tfrac{1}{2}\, v_3 \bar{w}_3$; $\tfrac{1}{2}\, \bar{v}_3\, \bar{w}_3$.

2. $u_2 0\, w_2$; $\bar{u}_2 0\, w_2$; $u_2 0\, \bar{w}_2$; $\bar{u}_2 0\, \bar{w}_2$.   4. $u_4 \tfrac{1}{2}\, w_4$; $u_4 \tfrac{1}{2}\, w_4$; $u_4 \tfrac{1}{2}\, \bar{w}_4$; $\bar{u}_4\, \tfrac{1}{2}\, \bar{w}_4$.

and

1. $0\, v_5 w_5$; $0\, \bar{v}_5 w_5$; $0\, v_5 \bar{w}_5$; $0\, \bar{v}_5\, \bar{w}_5$.   3. $\tfrac{1}{2}\, v_7 w_7$; $\tfrac{1}{2}\, \bar{v}_7 w_7$; $\tfrac{1}{2}\, v_7 \bar{w}_7$; $\tfrac{1}{2}\, \bar{v}_7\, \bar{w}_7$.

2. $u_6 0\, w_6$; $\bar{u}_6 0\, w_6$; $u_6 0\, \bar{w}_6$; $\bar{u}_6 0\, \bar{w}_6$.   4. $u_8 \tfrac{1}{2}\, w_8$; $\bar{u}_8 \tfrac{1}{2}\, w_8$; $u_8 \tfrac{1}{2}\, \bar{w}_8$; $\bar{u}_8\, \tfrac{1}{2}\, \bar{w}_8$.

A fairly good agreement of the observed and calculated intensities [2]) is obtained (Fig. 2), if the following parameters are attributed to the different atoms :

To the 16 S-atoms :

0 ; $v_1 = 0.13$; $w_1 = 0.15$. $\tfrac{1}{2}$; $v_3 = 0.33$; $w_3 = 0.15$.

$u_2 = 0.16$; 0 ; $w_2 = 0.25$. $u_4 = 0.38$; $\tfrac{1}{2}$; $w_4 = 0.25$.

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[1]) R. W. G. WYCKHOFF, The Analytical Expression of the Results of the Theory of Space-Groups, CARNEGIE-Publ., Washington, (1922), p. 59.

[2]) The calculation was only extended to the reflections designed in Fig. 2. as, for the higher order reflections and more complicated symbols the uncertainties become too great. The topography of the atoms in this structure can, therefore, only have the character of an approximotion, but evidently of a fairly good one.

To the 16 N-atoms :

$$0; \quad v_5 = 0.08; \quad w_5 = 0.30. \qquad \tfrac{1}{2}; \quad v_7 = 0.40; \quad w_7 = 0.30.$$
$$u_6 = 0.10; \quad 0; \quad w_6 = 0.10. \qquad u_8 = 0.42; \quad \tfrac{1}{2}; \quad w_8 = 0.10.$$

and the corresponding negative numbers, as expressed by the general symbols for the equivalent positions of each set mentioned above.
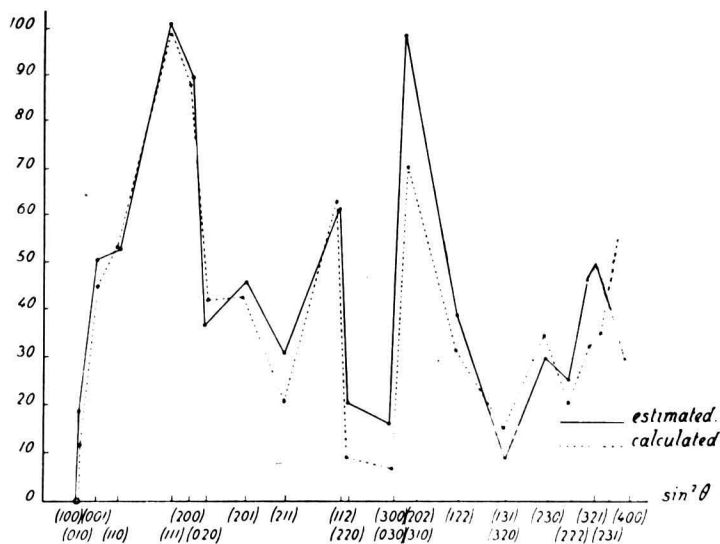

Fig. 2. Estimated and Calculated Intensities of the Diffraction-Lines of Nitrogen-tetrasulphide.

For the faces with more complicated symbols the agreement is less good, because the intensities observed are often the superposition of those of several planes whose diffraction-lines in the powder-spectrograms practically coincide.

The symmetry of each molecule N_4S_4 is C_{2v}; they are distributed within the elementary cell in such a way that the planes (100) and (010) are the symmetry-planes of each molecule and the c-axis is their binary symmetry-axis. There are 8 molecules placed on the edges of the cell which are parallel to the c-axis, and at some distance of the corners of the cell, — in total representing 2 molecules per cell; and two molecules are situated within the cell which are turned over 90° about their binary axis with respect to the first mentioned ones, while their top- and lower ends are interchanged in such a way, that the molecules become symmetrically placed with respect to the central mirror-plane, which is parallel to (001). The molecules, therefore, have the shape of polar, pyramidal arrangements, containing the four S-atoms in a kind of distorted tetrahedral configuration, and the four N-atoms in a similar, but not identical one, which is turned through 90° with respect to that of the S-atoms. Fig. 5 A can give some idea about this particular shape of the molecule, when seen along the c-axis.

51*

The atoms in these molecules are much more closely packed than in the case of $H_4N_4S_4$; if, — when the substance is melted, — they eventually might lose their polar binary axis, the rearrangement of the molecule then occurring would perhaps lead to a still closer and more completely tetrahedral packing of the atoms. It seems, however, very improbable, that in melting the substance, this configuration would be completely lost under formation of a "plane" ring-structure, — as, up to this moment, it was supposed to be present, as a consequence of purely chemical evidence and argumentation (see § 6).

II. Tetrahydro-Nitrogen-Tetrasulphide : $H_4S_4N_4$.

§ 6. This substance was prepared by MEUWSEN [1]) in *Munich* by the reduction of a solution of the *tetrasulphide* : N_4S_4 in benzene by means of an alcoholic solution of $SnCl_2$. The same product seems already to have been obtained by WÖLBLING [2]) in 1908 ; in contrast to N_4S_4 itself, it is a *colourless* substance, insoluble in most solvents, with the exception of alcohol, acetone, pyridine and piperidine. At 100° C. it becomes yellow and at 145° C. it is decomposed into ammonia and a red solution, probably consisting of sulphur in N_4S_4. Saponification by means of sodiumhydroxide yields ammonia and thiosulphate. The fact that LECHER's reaction [3]) gives a positive result and that, on treating it with formaldehyde, a compound : $(NS \cdot CH_2 \cdot OH)_4$ is generated, led MEUWSEN to the conclusion, that the hydrogen-atoms are directly linked to the sulphur-atoms. From the other fact that 16 atoms of bromine are taken up during the decomposition of the compound, he concludes that the sulphur in this compound is tetravalent, and that, therefore, a cyclic linkage of the nitrogen- and sulphur-atoms is proved, according to the formulae :

and : for the *tetrasulphide* itself.
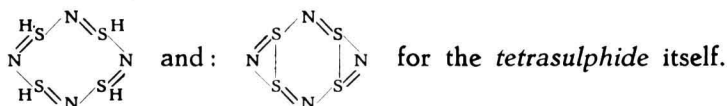
At first sight it might appear that the slow saponification of N_4S_4 with water, in the way observed by FORDOS and GÉLIS [4]) :

$$2 N_4S_4 + 15 H_2O = (NH_4)_2S_2O_3 + 2 (NH_4)_2S_3O_6 + 2 NH_3,$$

indicates, that three of the sulphur-atoms have a somewhat different function from the fourth one, — although no such a difference does manifest

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[1]) A. MEUWSEN, Ber. d. d. chem. Ges., **62**, (1930), 1959.

[2]) H. WÖLBLING, Z. f. anorg. Chem., **57**, (1908), 281.

[3]) H. LECHER and W. SIEFKEN, Ber. d. d. chem. Ges., **59**, (1927), 2600.

[4]) M. J. FORDOS and A. GÉLIS, Compt. rend. Paris. **31**, (1850), 702; Ann. de Chim. et Phys., (3). **32**, (1851), 391 260. About the cyclic formula for N_4S_4, conf. O. RUFF and E. GEISEL, loco cit., and the literature in ABEGG's Handbuch d. Anorg. Chem. **3**, 111, J. VON BRAUN, (1907), p. 101, etc.

itself in a number of other reactions of this substance. As Dr. MEUWSEN. however, in a private communication pointed out to us, this is *not* the case, because the *trithionate* is not formed as a primary, but only as a *secondary* reaction-product, according to the successive reactions :
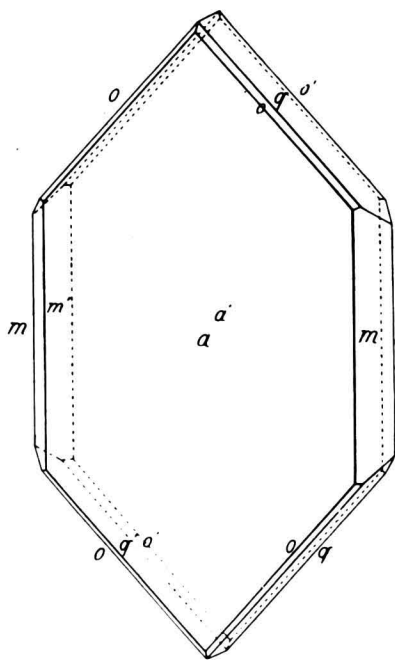
$$2\,N_4S_4 + 18\,H_2O = H_2S_2O_3 + 4\,H_2SO_3 + 8\,NH_3$$

and :

$$H_2S_2O_3 + 4\,H_2SO_3 = 2\,H_2S_3O_6 + 3\,H_2O.$$
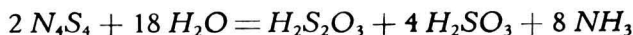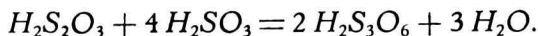
The second reaction is a most probable one, according to the investigations of FÖRSTER (Zeits. f. anorg. Chem., **157**, (1926), 45) ; and from these facts it, therefore, must be concluded, that the reaction observed by FORDOS and GÉLIS does *not* furnish any evidence against the equivalence of the four S-atoms in N_4S_4. The compound is a typically unsaturated one ; it can take up 4 and even 6 atoms of bromine, to form well crystallised addition-products. RUFF and GEISEL only obtained as reductionproducts : NH_3, SO_2, $H_2S_2O_4$, S and H_2S ; but MEUWSEN and WÖLBLING first succeeded in obtaining the *tetrahydro*-derivative just mentioned.

MEUWSEN now considers this reaction-product : $H_4N_4S_4$, as the *cyclic nitrile* of four molecules of the *sulphoxylic acid* : $H \cdot SO_2H$, and the *tetra-sulphide* : N_4S_4 itself as the *cyclic nitrile* of two molecules of *bisulphinic acid* : $HO_2S \cdot SO_2H$; in this way $H_4S_4N_4$ becomes analogous to *hydrocyanic acid* : HCN, and N_4S_4 to *dicyan* : C_2N_2.

§ 7.   At our request Dr. MEUWSEN kindly put a small quantity of the reductionproduct at our disposal, as well as some little crystals obtained from diluted alcohol. The crystals deposited from a dilute alcoholic solution were very small, thin colourless plates, which appeared to be soft and plastic, because of the presence of gliding planes parallel to the face {100}. The crystals (Fig. 3), however, yielded very sharp reflections, so that their crystalform could fairly well be determined.

The crystals are *orthorhombic,* and apparently have the symmetry of the *bipyramidal* class. The axial ratio was found to be :

$$a : b : c = 1.8202 : 1 : 1.1723 ;$$

calculated from the X-ray-measurements, it is :

Fig **3.** *Tetrahydro. Nitrogentetrasulphide*

$$a : b : c = 1.7869 : 1 : 1.1582,$$

which, — in connection with the small size of the measured crystals and the inevitable inaccuracies of the goniometric measurements, — can be considered as a fairly good agreement.

As we shall.see afterwards, it rather would be adviceable in this case to interchange the directions of the a-, and the c-axis, because by adopting the original orientation of the N_4S_4-crystals previously described, such an interchange in the case of the *tetrahydro*-derivative would give a more direct evidence of the close relationships between the atomic structures of the two compounds considered.

Forms observed : $a = \{100\}$, mostly predominant, yielding very sharp images ; $m = \{110\}$, also very well reflecting ; $o = \{111\}$, although narrow, yet giving beautiful reflections ; $q = \{011\}$, still narrower than o and yielding duller images. The habitus is that of hexagonally bordered, thin plates parallel to $\{100\}$, with a strong elongation in the direction of the c-axis. The angular values occasionally varied about 30′.

Angular Values:	*Observed:*		*Calculated:*	
$a : m = (100) : (110) =$*	61°	13	—	
$a : o = (100) : (111) =$*	67	19	—	
$m : m = (110) : (\bar{1}10) =$	57	34	57°	34′
$o : q = (111) : (011) =$	22	41	22	41
$o : o = (111) : (1\bar{1}1) =$	89	27	89	10
$o : o = (111) : (\bar{1}\bar{1}1) =$	143	28	143	13
$q : q = (011) : (0\bar{1}1) =$	98	58	99	4
$m : o = (110) : (111) =$	36	32	36	47

The plane of the optical axes is most probably parallel to $\{010\}$.

A distinct cleavability was not observed, but perhaps it is parallel to $\{100\}$; this face is also a gliding-plane of the crystals, which are easily smeared out in this direction.

The specific weight of the crystals at 20° C. was found to be : 1.88.

§ 8. Using a *copper*-anticathode, rotation-spectrograms were made by subsequently rotating the crystals round the c-, a- and b-axis. The identity-distances thus obtained, were improved by means of oscillation-spectrograms according to BRAGG [1]), on the face $\{100\}$, *calcite* being used as a standard-material for evaluating the right distance $d_{(100)} = 6.04$ Å. The exact values I, therefore, are : $I_c = 7.86$ Å ; $I_a = 12.08$ Å and $I_b = 6.76$ Å.

From the volume : 639.2 Å³ of the elementary cell and the molecular weight : $310,36.10^{-24}$ Gr., it follows that this cell contains a mass : $H_{16}S_{16}N_{16}$; the calculated density of the crystals is : 1.942.

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[1]) The spectrogram showed a second and a fourth order spectrum, the last being more intensive than the first.

Rotation-spectrograms were made by rotating the crystals over an angle of 60° (30° to both sides), with an exposure of 36—40 m. Amp. hours.

1. The spectrogram round [001] showed a splendid, completely symmetrical image, with more than 260 spots distributed over a principal and four accessory spectra. The images (α-radiation only) observed were :

Principal spectrum : **(020); *(400); (320); (510); (420); (520); **(040); (810); (050); (640); (550); (10.2.0); (260).

First Acc. Spectrum : **(011); (121); (321); *(031) or (421); (601); (431); (041) or (711); (821); (541); (351).

Second Acc. Spectrum : *(012); **(202) or (112); **(022); (322); *(512) or (422); *(602); (042) or (712); (342); (352); (922).

Third Acc. Spectrum : (113); *(123); (323); (513); (033); *(603); (433); (043) or (713); (823); (353); (453) or (10.03); (553).

Fourth Acc. Spectrum : *(304); *(314); *(414); *(504); (514) or (424); (524); (044) or (714); (344); (634); (814).

$I_c = 7.86$ Å.

Evidently the 2nd and 4th accessory spectra are more intense than the odd ones ; also the principal spectrum shows very intensive images.

2. The rotation-spectrogram round [100] was also very well developed and symmetrically built, showing small, but sharp spots. (Exposure : 40 m. Amp. hours ; *copper*-radiation ; angle of oscillation : (30° + 30°) = 60° ; more than 300 images).

$I_a = 12.08$ Å. The symbols of the α-images are :

Principal Spectrum : (002) ; **(012); *(022); (013); *(030); (004); *(024) and (033); (042) and (015); (034); (025) and (043); (050); *(016) and (035); (053); (054) and (061).

First Acc. Spectrum : (121); (103); *(122); (130); (133); (141); (142) and (115); (134); (125); (150); (106) and (151); (126); (107).

Second Acc. Spectrum : only two different images : **(212) and (242); and (215).

Third Acc. Spectrum : **(311); (321); (322); (330); (323); (333); (340); (341); (342) and (315); (334); (325); (350); (306) and (351); (316); (344) and (352); (326); (353); (345).

Fourth Acc. Spectrum : **(411); **(412); (403); (422); *(430); (423); **(404); (433); (442) and (415); (425) and (443); **(406) and (451); (445); (436).

Fifth Acc. Spectrum : (512); (521); (522); (530); (523); (533.); (541); (542) and (515); (534); (525) and (543); (506) and (551); (544) and (552); (526).

Sixth Acc. Spectrum : *(602); (622); (613).

Also here the spectra of even order were distinctly more intensive than those of odd order.

3. The rotation-spectrogram about [010] was a very good one, showing a principal and three accessory spectra.

$I_b = 6.76$ Å. The α-images observed were:

Principal Spectrum: **(102); *(202); *(302); (501); (502); (403) and (600); (204); *(404); (504) and (205); (900); *(605); (007); (207) and (904); (307); (805) and (11.0.1).

First Acc. Spectrum: **(011); **(112); (212); (312); (013); *(213); (412) and (510); **(413) and (610); **(612); *(711); (414) and (613); (514) and (215); (713) and (812); (515) and (911); (216) and (912); *(615); (10.1.1); (017); (317); (815) and (11.1.1); (417) and (11.1.2).

Second Acc. Spectrum: **(121); *(022); **(122); (420); (322); **(023); **(223); (422) and (520); *(323); **(522); *(423) and (620); (622); *(721); *(025) and (722); (524) and (225); (325); (723) and (822); *(724); *(625); *(027).

Third Acc. Spectrum: (132); **(332); (033); *(233); (432) and (530); (531); (333); *(630) and (433); *(632); (731); (434) and (633); (035) and (732); (534) and (235); *(831); (733) and (832); (930); (734); *(635).

The analysis of the spectrograms was made according to BERNAL's graphical method.

§ 9. Powderspectrograms were obtained with *copper-*, and with *iron-* radiation: (see Tables III and IV)

No. of Line:	$2l$ in m.M.:	Estim. Intens.:	Wave-length λ:	Angle θ:	$Sin^2 \theta$ (observed):	$Sin^2 \theta$ (calculated):	Indices (hkl):
						TABLE III.	
						Powder-Spectogram of $H_4 N_4 S_4$.	
1	29.12	3	α	7° 17′	0.0161	0.0162	(200)
2	34.44	4	α	8 37	0.0224	0.0226	(011)
3	41.35	2	β	10 22	0.0324	0.0314	(002) or (211)
4	45.95	10	α	11 35	0.0403	0.0384 or 0.0388	(002) or (211)
5	53.26	6⁺	α	13 20	0.0532	0.0519 or 0.0548	(020) or (202)
6	56.06	1	α	14 2	0.0588	0.0560	(120)
7	58.45	5	α	14 38	0.0638	0.0650	(400)
8	62.91	3	α	15 45	0.0737	0.0747 or 0.0752	(401) or (302)
9	67.97	4	α	17 1	0.0857	0.0876	(411)
10	71.24	4	α	17 50	0.0938	0.0929	(122)

TABLE III (*Continued*).

Powder-Spectogram of $H_4 N_4 S_4$.

No. of Line:	$2l$ in m.M.:	Estim. Intens.:	Wave-length λ:	Angle θ:	$Sin^2 \theta$ (observed):	$Sin^2 \theta$ (calculated):	Indices (hkl):
11	74.35	1	α	18° 37′	0.1019	0.1001	(013)
12	79.02	3	α	19 47	0.1146	0.1145 or 0.1162	(510) or (213)
13	83.30	1	α	20 52	0.1269	0.1272	(322)
14	87.30	1	α	21 52	0.1387	0.1366	(313) and (123)
15	92.20	2	α	23 5	0.1537	0.1547 or 0.1535	(004) or (520)
16	94.80	2	α	23 44	0.1620	0.1631 or 0.1650	(521), (331) or (413)
17	103.50	1	α	25 55	0.1910	0.1915 or 0.1901	(431) or (304)
18	105.95	1	α	26 32	0.1995	0.2015	(620)
19	120.20	1	α	30 6	0.2515	0.2504 or 0.2510	(142) or (720)

Radius of Camera: 57.2 m.M. Exposure: 80 m. Amp. hours.

Wave-length: $\lambda_\alpha = 1.540$ Å.; $\lambda_\beta = 1.388$ Å.

Quadratic Equation:

$$sin^2 \theta = 0.004063 \cdot h^2 + 0.012982 \cdot k^2 + 0.009671 \cdot l^2 \quad \ldots \ldots \ldots \ldots (\alpha)$$

$$sin^2 \theta = 0.003300 \cdot h^2 + 0.010546 \cdot k^2 + 0.007856 \cdot l^2 \quad \ldots \ldots \ldots \ldots (\beta)$$

Parameters of the Lattice:

$$a_0 = 12.08 \text{ Å}; \quad b_0 = 6.76 \text{ Å}; \quad c_0 = 7.86 \text{ Å}.$$

Specific Weight: 1.94. Simple rhombic lattice; 4 molecules pro elem. cell.

TABLE IV.

Powder-Spectogram of $H_4 N_4 S_4$.

No. of Line:	$2l$ in m.M.:	Estim. Intens.:	Wave-length λ:	Angle θ:	$Sin^2 \theta$ (observed):	$Sin^2 \theta$ (calculated):	Indices (hkl):
1	36.6	3	α	9° 10′	0.0254	0.0257	(200)
2	38.7	1	β	9 42	0.0284	0.0292	(011)
3	43.6	6	α	10 54	0.0357	0.0357	(011)
4	46.8	1	α	11 43	0.0412	0.0409	(201)
5	51.5	1	β	12 54	0.0498	0.0497	(002) and (211)
6	53.9	1	β	13 20	0.0545	0.0501	(102)
7	56.7	8	α	14 12	0.0602	0.0611 and 0.0614	(002) and (211)
8	59.2	9−	α	14 49	0.0654	0.0675	(102)

No. of Line:	2l in mM.:	Estim. Intens.:	Wave-length: λ:	Angle θ:		Sin² θ (observed):	Sin² θ (calculated);	Indices (hkl):
							TABLE IV (Continued).	
							Powder-Spectogram of $H_4 N_4 S_4$.	
9	67.0	4	"	16°	47'	0.0834	0.0821	(020)
10	68.0	4+	"	17	1	0.0856	0.0869	(202)
11	70.9	2	"	17	45	0.0929	0.0885 or 0.0971	(120) or (021)
12	74.2	4	"	18	35	0.1016	0.1028	(400)
13	79.8	3	"	19	58	0.1166	0.1181	(401)
14	86.4	3	"	21	38	0.1359	0.1386	(411)
15	90.6	3	"	22	41	0.1487	0.1469	(122)
16	94.0	1	"	23	32	0.1594	0.1581	(013)
17	100.8	2	"	25	14	0.1818	0.1811 or 0.1838	(510) or (213)
18	106.9	1	"	26	46	0.2028	0.2011	(322)
19	110.9	1	"	27	46	0.2170	0.2159 or 0.2161	(313) or (123)
20	118.4	1		29	39	0.2447	0.2446	(004)
21	122.3	1	"	30	37	0.2594	0.2580	(331) or (413)
22	124.0	1	"	31	3	0.2660	0.2651	(014)
23	133.0	3	"	33	18	0.3014	0.3004 or 0.3028	(304) or (431)
24	136.6	2	"	34	13	0.3162	0.3187	(620)
25	139.8	1	"	35	0	0.3290	0.3267 or 0.3288	(024) or (133)
26	143.7	1	"	35	59	0.3452	0.3453	(530)
27	157.6	2	"	39	28	0.4041	0.4028 or 0.4052	(015) or (504)
28	160.9	1	"	40	17	0.4181	0.4153 or 0.4161	(242) or (630)
29	165.8	1	"	41	31	0.4394	0.4401	(305)
30	176.1	1	"	44	6	0.4843	0.4851	(405)
31	214.3	1	"	53	42	0.6496	0.6508	(053)
32	221.0	1	"	55	20	0.6765	0.6760	(444)

Radius of Camera: 57.2 m.M. Exposure: 40 m. Amp. hours.

Wave-Length: $\lambda_\alpha = 1.9366$ Å.; $\lambda_\beta = 1.7527$ Å.

Quadratic Equation:

$$sin^2 \theta = 0.006425 . h^2 + 0.020531 . k^2 + 0.015293 . l^2 \quad \dots \dots \dots \quad (\alpha)$$

$$sin^2 \theta = 0.005266 . h^2 + 0.01683 . k^2 + 0.012534 . l^2 \quad \dots \dots \dots \quad (\beta)$$

Parameter of the Lattice: $a_0 = 12.08$ Å.; $b_0 = 6.76$ A.; $c_0 = 7.86$ Å.

Specific Weight: 1.94. The cell contains 4 molecules $H_4 N_4 S_4$: simple rhombic lattice.

§ 10.   From all these data we can deduce the following survey of the intensities of the most important diffraction-images ; the triplets indicated between brackets : ( ) are those that have the intensity = zero ; they are, therefore, absent. Triplets indicated with ** have very strong intensities, those with * rather large ones, the other ones show only weak intensities.

I. $c = 0$.					
(100)	* 200	(300)	**(400)	(500)	*600
(110)	(210)	(310)	(410)	510	*610
(120)	(220)	320	420	520	620
(130)	(230)	330	* 430	530	*630
(140)	(240)	340		(540)	640
150	(250)	350		550	
	260				
$h=1$	$h=2$	$h=3$	$h=4$	$h=5$	$h=6$

II. $a = 0$.				
(010)	* 020	030	*040	050
**011	(021)	*031	041	(051)
* 012	*(022)	*032	042	(052)
* 013	*(023)	033	043	053
(014)	024	034	044	054
015	025	035		
* 016	026	036		
017	027			
$k=1$	$k=2$	$k=3$	$k=4$	$k=5$

III. $b = 0$.						
(001)	*002	(003)	*004	005	006	007
(101)	*102	103	(104)	(105)	106	107
(201)	**202	(203)	204	(205)	(206)	207
* 301	*302	303	304	(305)	306	307
* 401	(402)	(403)	*404	(405)	* 406	
501	502	(503)	504	(505)	506	
601	*602	603	604	* 605	606	
* 701	702					
$l=1$	$l=2$	$l=3$	$l=4$	$l=5$	$l=6$	$l=7$

Hence in this case, there are much more extinctions than in the case of N_4S_4.

The odd orders of (100) are also absent in the rotation-spectrograms; but the ninth order: (900) finally appears with a small intensity. This makes it probable that, — because also on {010} and {001} the odd order spectra are lacking or are only very weak in the higher orders, — the face {100} of the structure is centred, or *almost* centred, while in the direction of the *a-axis* a molecule is shifted along this axis over almost $\frac{1}{2}a$. These facts are corroborated by the circumstance, that, while (011) has a great intensity, (101) is absent; but (202) and (404) are very intensive, as well as (102), and that also (110) is absent. Of the four molecules in the elementary cell, two are in the same position; while the two molecules, the one of which is not in, but near to the centre of the face (100), the other one being shifted in the direction of the *a-axis* perpendicular to the centre of the face (100), over nearly $\frac{1}{2}a$, — must both have a different orientation from the other ones. Also the absence of the reflection (111) is in agreement with these views about the particular way of arrangement just explained.

Although certainly the structure of $H_4N_4S_4$ is a "molecular" arrangement, we have, — exactly as in the case of N_4S_4, — *not* deduced this structure by considering the possible arrangement of these four (2 + 2) "molecules", but by considering the characteristic positions of the 2×8 S-atoms and of the 2×8 N-atoms themselves. The problem then is: to attribute such co-ordinates to these 32 atoms, as to account for the observed intensities of the diffraction-images $\{h\ k\ l\}$.

After the places of the 16 S-atoms and then those of the 16 N-atoms within the elementary cell are fixed in this way, it afterwards can be tried to find out, whether larger groups of them are so arranged, as to constitute "molecular" aggregates. Of course, chemical considerations can be of some use in this, as they may give us some indications about the way in which different atoms are linked to each other; but the agreement in purely geometrical respect must be the primary condition to be fulfilled.

The determination of the co-ordinates of the different atoms meets with serious difficulties also in this case.

If we take the bipyramidal symmetry for granted, then the structure only can have the symmetry of the space-group V_H^1 formerly discussed.

Neither the attribution of the 16 atoms of the same kind to 16 one-fold positions, — which are not present, — nor that of placing them in 8 two-fold positions of the kinds allowable in this space-group [1]) can account for the particularities of the intensity-phenomena; neither of the relatively great intensity of (011), nor, — if the two-fold places recorded by

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1) R. W. G. WYCKOFF, The Analytical Expression of the Results of the Theory of Spacegroups, (1922), p. 59.

WYCKOFF [1]) under (i) to (l) be chosen, — of the pecularities of the reflections on the faces (010) and (001).

However, such difficulties do not arise, if the 16 S-atoms and the 16 N-atoms are distributed over *four*-fold positions, and if the identity of the four molecules $H_4N_4S_4$ are given up in so far, that to two of them another orientation is given than to the two others, — they, moreover, being shifted with respect to the others over a distance of almost $\frac{1}{2} a$. The shift cannot exactly be $\frac{1}{2} a$, because of the fact that the distances $d_{(100)}$, $d_{(010)}$, and $d_{(001)}$ appear only *approximately* halved, *not all* odd orders on the faces (100), (010), (001) being absent, although they are always very weak in comparison with the reflections of the second and fourth orders.

The calculation of the intensities was performed in the usual way, the diffractive power of the N- and the S-atoms being assumed proportional to their atomic numbers. Because of the symmetry, the term of the structural factor S containing the sinuses, is always $=$ zero.

The best agreement of the calculated and observed intensities was obtained, when attributing to the different atoms the following values of the parameters u, v, and w in the general symbols:

1. $u_1 v_1 \frac{1}{2}$; $\bar{u}_1 v_1 \frac{1}{2}$; $u_1 \bar{v}_1 \frac{1}{2}$; $\bar{u}_1 \bar{v}_1 \frac{1}{2}$. | 3. $u_3 0 w_3$; $\bar{u}_3 0 w_3$; $u_3 0 \bar{w}_3$; $\bar{u}_3 0 \bar{w}_3$.
2. $u_2 v_2 0$; $\bar{u}_2 v_2 0$; $u_2 \bar{v}_2 0$; $\bar{u}_2 \bar{v}_2 0$. | 4. $u_4 \frac{1}{2} w_4$; $\bar{u}_4 \frac{1}{2} w_4$; $u_4 \frac{1}{2} \bar{w}_4$; $\bar{u}_4 \frac{1}{2} \bar{w}_4$.

and :

1. $u_5 0 w_5$; $\bar{u}_5 0 w_5$; $u_5 0 \bar{w}_5$; $\bar{u}_5 0 \bar{w}_5$. | 3. $u_7 v_7 0$; $\bar{u}_7 v_7 0$; $u_7 \bar{v}_7 0$; $\bar{u}_7 \bar{v}_7 0$.
2. $u_6 \frac{1}{2} w_6$; $\bar{u}_6 \frac{1}{2} w_6$; $u_6 \frac{1}{2} \bar{w}_6$; $\bar{u}_6 \frac{1}{2} \bar{w}_6$. | 4. $u_8 v_8 \frac{1}{2}$; $\bar{u}_8 v_8 \frac{1}{2}$; $u_8 \bar{v}_8 \frac{1}{2}$; $\bar{u}_8 \bar{v}_8 \frac{1}{2}$.

   a. To the 16 *Sulphur*-atoms :

$u_1 = 0.15$; $v_1 = 0.30$; $\frac{1}{2}$ $u_3 = 0.35$; 0; $w_3 = 0.18$.

$u_2 = 0.15$; $v_2 = 0.16$; 0 $u_4 = 0.35$; $\frac{1}{2}$; $w_4 = 0.36$

and the corresponding negative values, as denoted by the general symbols for the four equivalent positions of each set.

   b. To the 16 *Nitrogen*-atoms :

$u_5 = 0.15$; 0; $w_5 = 0.17$ $u_7 = 0.35$; $v_7 = 0.20$; 0.

$u_6 = 0.15$; $\frac{1}{2}$; $w_6 = 0.33$ $u_8 = 0.35$; $v_8 = 0.30$; $\frac{1}{2}$

and the corresponding negative values, as denoted by the general symbols mentioned above.

§ 11. Qualitatively the calculated intensities are sufficiently well in accordance with the observed ones in so far, that reflections of high intensity also appear as such amongst the calculated ones, while the extinctions or very weak reflections really obtain very small intensities. The ratio of the intensities is not so well expressed, — a fact, which for a good deal must be ascribed to the inexactness of their visual estimation. A shift

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[1]) Ibidem, p. 59.

of some atoms over as little as 0.02 Å, often causes a very considerable change of the intensity-ratio of some planes $\{h\ k\ l\}$.

Fig. 4 gives a graphical representation of the calculated (broken line) and of the observed (full line) intensities. With the exception of the still too small value of (102), the agreement is a fairly sufficient one, if the fact be taken into account, that no less than 16 parameters had to be determined and that a very small shift of one of the atoms causes considerable variations of the intensities.

Under these circumstances it seems to be a hopeless task to try further to improve the agreement between the calculated and the observed intensities by a continued change of the parameter-values, because the number of possible combinations is much too great for such an attempt. In every case the parameters mentioned seem to give a very fair approximation of the real ones.

The proper symmetry of the "molecular" aggregates $H_4N_4S_4$ is C_{2v}; they thus possess a binary axis parallel to the a-axis and two planes of symmetry passing through it, which symmetry-planes are parallel to the (010) and (001)-faces, and in which each time two S-atoms (or N-atoms) are situated in pairs. The *diameters* of the spheres representing the S- and
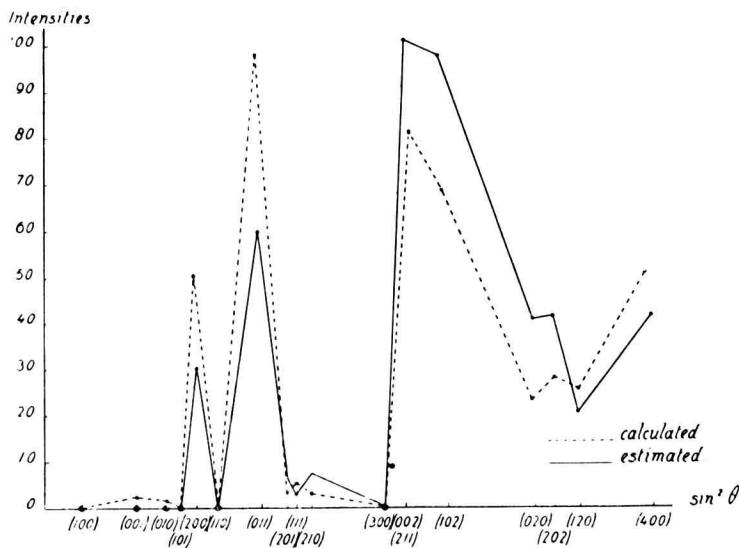

Fig 4. Estimated and Calculated Intensities of the Diffraction Image of $H_4N_4S_4$.

N-atoms in the structure are taken as : 2.18 Å and 1.4 Å respectively. Eight molecules are thus situated on the edges of the cell which are parallel to the a-axis, at some distances from the corners ; and two molecules are placed within the cell, on the a-axis passing through the centres of the faces (100) and ($\bar{1}$00), and they are shifted along this axis. The H-atoms (diameter ;
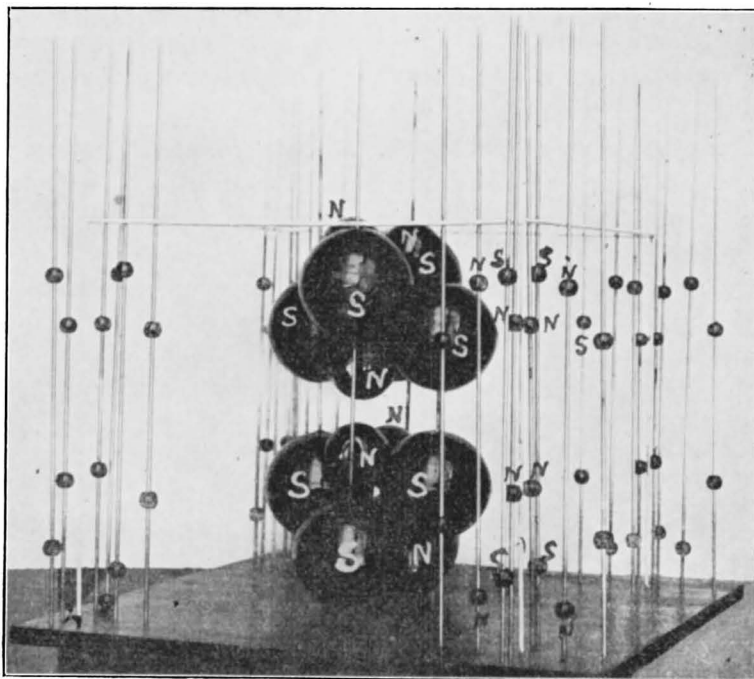
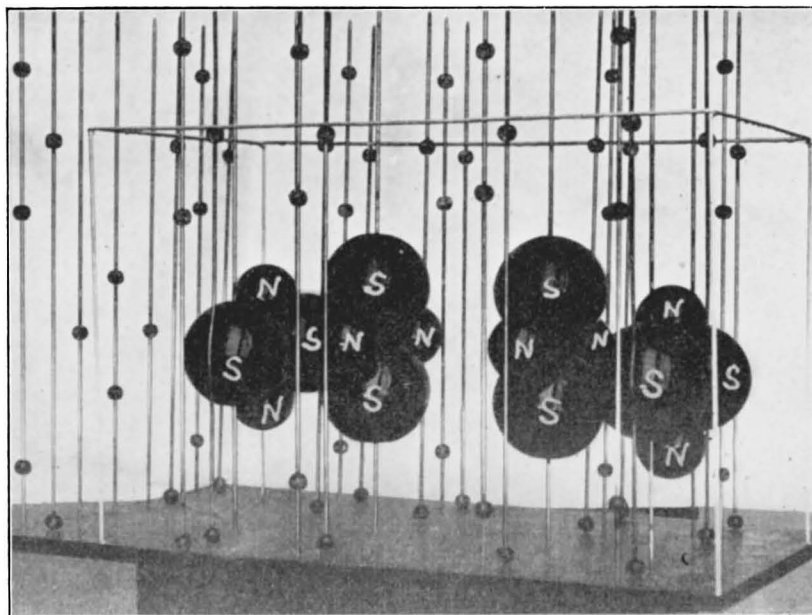Fig. 5ᴬ. Configuration of Nitrogentetrasulphide

Fig. 5ᴮ. Configuration of Tetrahydronitrogentetrasulphide.

1.0 Å) are attached to the S-atoms ; but their places could not be accurately determined, because of their weak diffracting power. They are most probably situated in the direction of the a-axis, as this appears chiefly to be enlarged in comparison with the dimensions of the cell of N_4S_4. The orientation of the two sets of molecules $H_4N_4S_4$ is such, that the one kind is, with respect to the other kind turned through an angle of 90° round the direction of the a-axis, while simultaneously the front- and backside of each molecule is interchanged. Both sets are *continued* throughout the whole structure by their repeatedly being reflected in the symmetry-planes parallel to (100) ; etc.

Evidently, also in this case, *no* "plane" cyclic structure is present within the molecule $H_4N_4S_4$: the usual chemical formula most probably gives only a rather rudimentary representation of the mutual positions of the atoms within the molecule, — although, of course, the stereometrical arrangement here determined, may not be assumed to be completely preserved, when the substance is brought into the liquid or the gaseous state. Most conspicuous is the fact, that by the introduction of the 4 *hydrogen*-atoms into the molecule N_4S_4, the two layers of $(2S + 2N)$-atoms are thrown farther apart than in the original molecule : also this fact makes it probable, that the hydrogen-atoms are really inserted into the molecule in the direction of the a-axis of $H_4N_4S_4$ and attached to the *sulphur*-atoms.

The arrangement of the *sulphur*- and *nitrogen*-atoms in the individual molecules of N_4S_4, as seen in the direction of the c-axis, and that in the molecules of $H_4N_4S_4$ as seen in the direction of the a-axis, is represented in
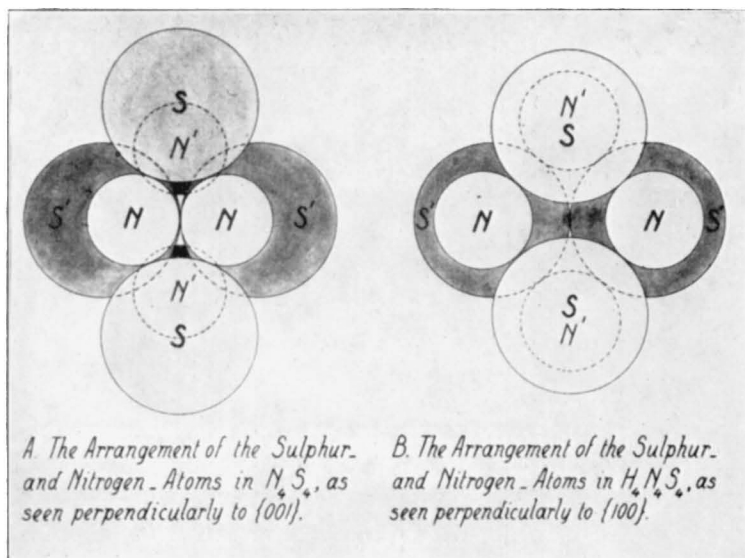

A. The Arrangement of the Sulphur- and Nitrogen-Atoms in N_4S_4, as seen perpendicularly to {001}.

B. The Arrangement of the Sulphur- and Nitrogen-Atoms in $H_4N_4S_4$, as seen perpendicularly to {100}.

Fig. 6.

Fig. 5 A, respectively in Fig. 5 B for the purpose of comparison[1]); more-over, in Fig. 6, this configuration is represented in projection on the faces (001) and (100) respectively.

Finally it may be remarked here, that the close relationship of the structures of N_4S_4 and of $H_4N_4S_4$ can more evidently be brought about by interchanging the directions of the a-, and of the c-axis in one of the two structures. It is then immediately seen, that the packing is looser in $H_4N_4S_4$, than it is in N_4S_4.

<div align="center">Groningen, Laboratory for Inorganic and
Physical Chemistry of the University.</div>

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[1]) In these Figures, only the atoms of the two molecules which are situated *within* the interior part of the cell are fully represented by means of spheres of suitable dimensions; of the other two molecules only the *centres* of these spheres are indicated by means of coloured beads.