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The Crystal Structure of $N_4S_4H_4$

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An X-ray crystallographic study of $N_4S_4H_4$ has been carried out. The analysis shows that that the molecule has the form of a puckered eight-membered ring with alternating sulphur and nitrogen atoms. The positions of the hydrogen atoms have not been determined.

Several authors have regarded as a plausible structure of $N_4S_4H_4$ one which is based on an 8-membered ring with alternating sulphur and nitrogen atoms [1,2]. For the attachment of the hydrogen atoms two different opinions have been held. Some chemical evidence [1,5] is said to point in favour of a structure with hydrogen atoms linked to sulphur atoms. A study of the infrared spectrum [6] indicates, however, the presence of NH rather than SH bonds in the molecule.

The aim of the present investigation is to establish the arrangement of sulphur and nitrogen atoms in the molecule by means of X-ray crystallographic methods. It has not been possible or even tried to locate hydrogen atoms. A crystal structure determination of the same substance has been performed previously by Jaeger and Zanstra [3], using rotation and powder X-ray diagrams. We have, however, not been able to find correspondence between some of their data and results and ours.

The substance was prepared by the method described by Meuwsen. N_4S_4 in benzene was reduced by stannous chloride in alcoholic solution. From acetone needle-shaped crystals of $N_4S_4H_4$ were obtained, but also small bipyramidal plates were observed.

Oscillation and rotation X-ray diagrams showed that $N_4S_4H_4$ crystallizes in the orthorhombic system. The unit cell dimensions were found to be $a = 6.75$ Å, $b = 7.97$ Å, $c = 12.19$ Å. These values are assumed to be accurate to within one half per cent. With four molecules in the unit cell the dimensions lead to a calculated density of 1.907 gcm^{-3} which compares favourably with the observed value [3] of 1.88 gcm^{-3}.

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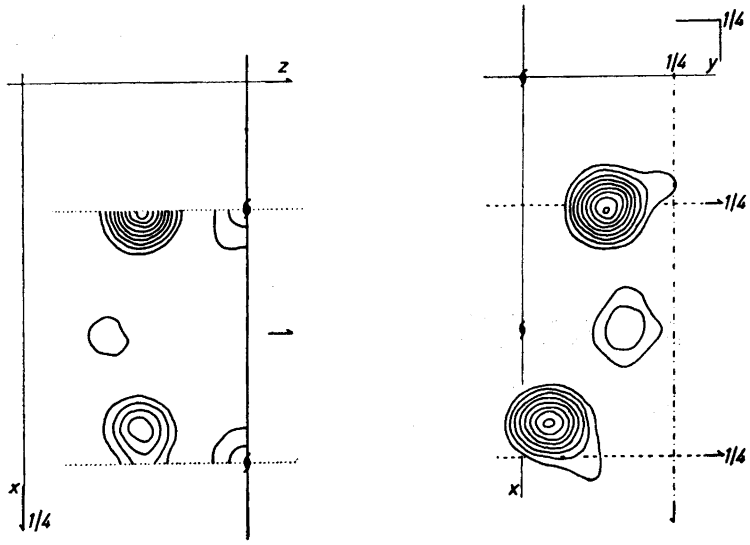

Figs. 1 and 2. Projections of the asymmetric unit of $N_4S_4H_4$ on (001) and (010), respectively. Electron density maps with interval between contour lines corresponding to 10 electrons per Å^2, the lowest lying at 10 electrons per Å^2.

Weissenberg diagrams, taken with Cu-*K* radiation show extinctions of reflexions characteristic of the space groups *Pbnm* or *Pbn*. The Wilson ratio $\langle|F|\rangle^2 / \langle|F|^2\rangle$ was computed for seven different sets of reflexions lying within concentric areas in reciprocal *h0l* plane. The mean value of the ratio was found to be 0.63, which indicates the most symmetric space group *Pbnm*. With four molecules in the unit cell this space group requires two halves of a molecule to be crystallographically equivalent.

Intensities of *h0l* and *hk*0 reflexions were estimated visually by means of a standard scale, using the multiple film technique. Patterson projections were computed and found to be compatible with a structure based on an 8-membered ring with alternating S and N atoms and having the point symmetry 4 *mm*. If this is the main feature of the structure one of the symmetry planes of the molecule has to coincide with the symmetry plane of the space group.

A model was tentatively assumed with N—S distance equal to 1.77 Å and with the angles N—S—N and S—N—S equal to 105° and 109°, respectively. Patterson projections served to locate such a model in the unit cell with a satisfactory degree of correspondence between observed and calculated structure factors. Fourier projections on (001) and (010) planes were computed. The contour maps are shown in Figs. 1 and 2. The interval between contour lines corresponds to 10 electrons per Å^2.

From these electron density maps rather reliable coordinates of sulphur atoms can be derived. Only one nitrogen atom gives rise to a well separated peak. The other two nitrogen atoms of the molecule cannot be located accu-

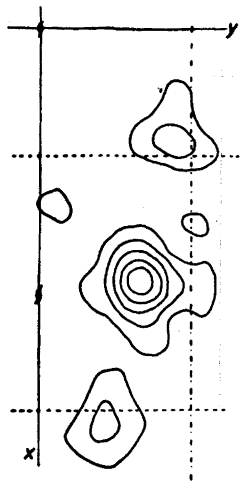

Fig. 3. Difference electron density projection on (001), amplitudes being $F_0 - F_s$. Interval between contour lines corresponding to 3 electrons per Å², the lowest lying at 3 electrons per Å².

rately due to overlap from other atoms in the projections. In order to determine the coordinates of these nitrogen atoms a difference synthesis $F_0 - F_s$ was performed in the projections on (001), F_s being the calculated contribution of the sulphur atoms to the structure factor. In Fig. 3 the resulting difference electron density map is reproduced. From this map the x and y coordinates of the nitrogen atoms were derived. Figs. 4 and 5 show the arrangement of the molecules in the unit cell.

In Table 1 the final coordinates are listed. These coordinates lead to four independent determinations of the N—S distance of the magnitude 1.65 ± 0.02 Å and further to three independent values of the angle S—N—S lying in the range 122° ± 3° and two values of the angle N—S—N within 109° ± 1°.

In Table 2 observed and calculated structure factors are given. The calculated values include temperature factors B equal to 3.00 and 3.65 Å² for the projections on (010) and (001), respectively. No correction for absorption has

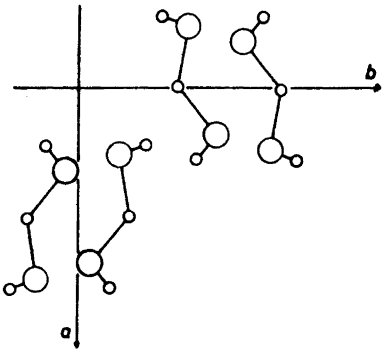

Fig. 4. Projection of the structure of $N_4S_4H_4$ along the c-axis.

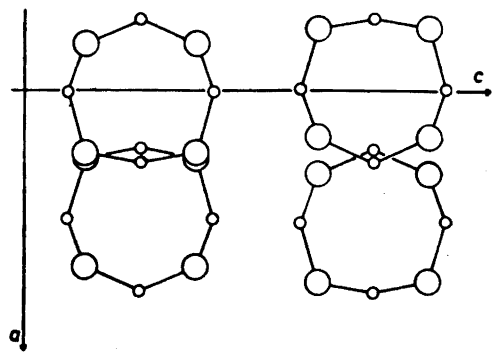

Fig. 5. Projection of the structure of $N_4S_4H_4$ along the b-axis.

Table 1. Coordinates of sulphur and nitrogen atoms.

	x	*y*	*z*
S_1	0.259	0.137	0.131
S_4	0.680	0.043	0.131
N_1	0.221	0.225	0.250
N_3	0.774	0.108	0.250
N_4	0.494	0.171	0.094

been made. Nor has the contribution of hydrogen atoms to the structure factors been considered. The 'reliability index' $R = \Sigma||F_0| - |F_c|| / \Sigma |F_0|$ is found to be 0.13 for the projections on (010) and 0.17 for the projection on (001).

Table 2. Observed and calculated structure factors. (One eighth of absolute values.)

hkl	$\|F_0\|$	$\|F_c\|$	*hkl*	$\|F_0\|$	$\|F_c\|$	*hkl*	$\|F_0\|$	$\|F_c\|$
020	3.1	4.0	470	1.7	2.4	1 011	0	0.2
040	5.4	5.2	480	1.6	1.5	1 013	0	0.2
060	2.5	2.1	490	0.2	0.5	202	7.3	6.9
080	1.4	0.8	510	4.8	5.0	204	8.5	8.8
0 100	1.6	2.0	520	5.1	5.6	206	2.1	2.6
110	7.2	8.5	530	0.6	0.4	208	10.5	10.7
120	4.3	4.4	540	0	0.4	2 010	4.5	5.0
130	1.4	1.1	550	0	0.6	2 012	4.8	4.5
140	8.4	9.5	560	0.9	0.3	2 014	1.6	1.6
150	1.3	1.5	570	0.4	0.4	301	4.1	4.5
160	6.9	7.3	580	1.3	1.4	303	3.2	3.4
170	0.6	0.1	600	0.9	0.3	305	3.7	4.3
180	0	0.6	610	0	0.5	307	2.1	1.9
190	2.6	1.2	620	2.8	2.6	309	2.8	3.1
1 100	0.7	0.8	630	0	0.2	3 011	1.3	0.9
200	15.1	18.2	640	3.7	3.2	3 013	2.0	1.7
210	1.4	1.3	650	1.9	2.1	402	1.2	1.3
220	4.8	4.6	660	0.5	0.2	404	4.2	4.6
230	2.6	3.2	670	0.3	0.8	406	1.0	1.8
240	3.7	3.6	710	0	0.3	408	3.4	4.2
250	4.3	5.0	720	3.2	3.1	4 010	0.9	0.9
260	0	0.4	730	0	0.1	4 012	0.6	0.8
270	1.7	2.4	740	1.1	1.2	501	5.5	6.4
280	1.9	1.9	750	0.6	0.5	503	5.1	5.4
290	0	0.6	800	0.6	0.5	505	4.8	5.0
310	6.2	6.7	810	0.4	0.6	507	2.7	3.1
320	5.0	5.3	820	2.2	1.7	509	3.1	4.2
330	6.2	6.1	830	1.1	1.1	5 011	1.8	1.4
340	3.8	3.4	840	0.8	1.8	602	1.0	1.1
350	0	0.3	002	5.7	5.7	604	0.5	1.1
360	3.7	3.5	004	17.5	20.1	606	0.6	0.4
370	0	0.6	006	3.9	2.0	608	1.1	0.5
380	0.7	0.6	008	15.0	14.3	6 010	1.1	0.9
390	0.3	0.9	0 010	3.3	3.7	701	3.7	4.3
400	9.5	9.1	0 012	5.8	4.8	703	3.2	3.5
410	1.5	1.1	0 014	1.2	1.6	705	4.2	4.5
420	3.4	3.3	101	1.0	1.0	707	1.9	2.0
430	2.2	2.2	103	0.8	0.9	709	2.6	3.4
440	5.7	5.3	105	0.8	0.7	802	0	0.1
450	4.2	4.7	107	0.6	0.4	804	0	0.2
460	1.4	1.7	109	0.5	0.4	806	0	0.6

In order to establish the position of the hydrogen atoms in the molecule it would be of interest to study derivatives in which hydrogen is replaced by a heavier atom or group. The formaldehyde derivative $N_4S_4(CH_2OH)_4$ has been prepared according to Meuwsen. X-Ray diagrams show that this compound belongs to the space group *Pbca* with axial lengths 12.0 Å, 13.1 Å and 15.8 Å. The observed density is 1.55 gcm^{-3} whereas the calculated density assuming eight molecules in the unit cell is 1.74 gcm^{-3}. A more detailed crystallographic study of this compound has not been carried out. The preparation of a compound $N_4S_4F_4$ has been reported [4] and the compound is said to belong to the space group $P\ \bar{4}\ 2_1c$ with two molecules in the unit cell. The point symmetry of the molecule must then necessarily be $\bar{4}$. Assuming that the structure of this molecules also is based on an 8-membered ring, this point symmetry leads to a structure different from that found for $N_4S_4H_4$. It will be of interest to see a more detailed analysis of the structure of the fluorine derivative.

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