

complexes. It has been demonstrated that the very stable $(M^+.4TU)_n$ coordination column with symmetry $4/m$ is not an essential structural unit. A better criterion is that these complexes will form whenever any three-dimensional arrangement of ions and dipoles in the same crystal gives a higher intrinsically negative lattice energy than the sum of the lattice energies of the separate crystals. These quantities are exactly calculable and a programme is under way to investigate the electrostatic stability of various structure types by numerical methods.

References

- BOEYENS, J. C. A. (1968a). *Acta Cryst.* B24, 199.
 BOEYENS, J. C. A. (1968b). *Acta Cryst.* B24, 1191.
 BOEYENS, J. C. A. & HERBSTSTEIN, F. H. (1967). *Inorg. Chem.* 6, 1408.
International Tables for X-ray Crystallography (1952). Vol. I, p. 152. Birmingham: Kynoch Press.
 PIMENTEL, G. C. & MCCLELLAN, A. L. (1960). *The Hydrogen Bond*, p. 289. San Francisco: Freeman.
 TRUTER, M. R. (1967). *Acta Cryst.* 22, 556.
 VERHOEF, L. H. W. & BOEYENS, J. C. A. (1968). *Acta Cryst.* B24, 1262.

Acta Cryst. (1969). B25, 611

The Structure of Three Isomers $S_6(NH)_2$

BY J. C. VAN DE GRAMPPEL AND AAFJE VOS

Laboratorium voor Structuurchemie, Rijksuniversiteit Groningen, Bloemsingel 10, Groningen, The Netherlands

(Received 19 February 1968)

The three known isomers of $S_6(NH)_2$ were studied. Two-dimensional X-ray work showed one of the isomers, $S_6(NH)_2$ II with m.p. $153^\circ C$, to be identical with the compound $S_6(NH)_2$ studied by Weiss (*Z. anorg. chem.* (1960) 305, 190). The four molecules in the orthorhombic unit cell with $a=7.87$, $b=12.86$, $c=7.38$ Å lie at special positions m in space group $Pnma$. They contain eight-membered puckered rings of sulphur and nitrogen atoms (crown conformation) with the latter in the 1,5 positions.

The crystals of $S_6(NH)_2$ I (m.p. $130^\circ C$) are monoclinic with $a=8.054$, $b=12.522$, $c=8.368$ Å, $\beta=114.45^\circ$, space group $P2/n$. The unit cell contains two independent pairs of molecules lying at special positions with symmetry 2. The crystal structure was determined from a three-dimensional Patterson synthesis and a difference synthesis. Refinement by anisotropic least-squares analysis of 1244 independent reflexions with non-zero intensity gave an index R of 0.048. The molecules are eight-membered rings in crown conformation. The NH groups appeared to be in the 1,4 positions. Average bond lengths and angles with e.s.d.'s for the individual values in parentheses are S-S=2.048 (0.006), N-S=1.724 (0.010) Å, $\angle SNS=119.1$ (0.5), $\angle NSS=110.1$ (0.4) and $\angle SSS=107.3$ (0.2)°.

For $S_6(NH)_2$ III only preliminary X-ray work was done. Chemical considerations and comparison of the infrared and mass spectra of the three isomers very strongly indicated that $S_6(NH)_2$ III (m.p. $123^\circ C$, space group $Pbca$, $a=8.18$, $b=12.84$, $c=14.06$ Å, $Z=8$ formula units) is cyclohexasulphur-1,3-diimide.

Introduction

From the reaction mixture of S_2Cl_2 and NH_3 several sulphur imides have been isolated: Goehring, Herb & Koch (1951) prepared a compound with formula S_7NH , Weiss (1959) obtained a solid with composition $S_6(NH)_2$ in addition to S_7NH and some other products, Tavs, Schulz-Steinen & Colchester (1963) and Heal (1963) showed by careful absorption chromatography

that not only one, but three, compounds $S_6(NH)_2$ were formed during the reaction. Later, Heal & Kane (1964) succeeded in isolating two isomers with composition $S_5(NH)_3$. As all these sulphur imides obey the general formula $S_{8-x}(NH)_x$, it was supposed that they contained eight-membered rings as in S_8 , with one or more of the sulphur atoms replaced by NH groups. A similar structure was assumed for $S_4(NH)_4$ which had been prepared by reduction of S_4N_4 by $SnCl_2$ in methanol (Meuwesen & Lösel, 1953). For some compounds, e.g. S_7NH (Weiss, 1960; Weiss & Neubert, 1965) and $S_4(NH)_4$ (Lund & Svendsen, 1957; Sass & Donohue, 1958), the hypothesis was confirmed by an X-ray study of the crystal structures. In both cases the shape of the ring is analogous to the crown shape observed in orthorhombic sulphur. In $S_4(NH)_4$ the ring appeared to consist of alternating sulphur and nitrogen atoms.

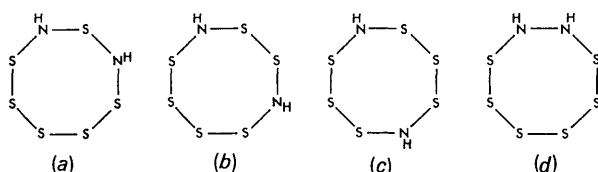


Fig. 1. Possible molecular structures for the isomers $S_6(NH)_2$.

For compounds with composition $S_6(NH)_2$ four structures based on the S_8 ring [(a) to (d) in Fig. 1] are possible. Chemical arguments show, however, that the isomer with structure (d) is not likely to be prepared from S_2Cl_2 and NH_3 . For the three isomers obtained, three structures (a) to (c) are thus available. The isomers were characterized by their respective melting points: 123, 130 and 153°C. Measurements of several physical constants by Tavs *et al.* (1963) and Heal (1963) did not yield conclusive evidence on the structure of each of the isomers. The present authors were therefore asked to determine the structures by means of X-ray diffraction. Two-dimensional X-ray work showed that the compound isolated by Weiss, for which a three-dimensional X-ray study had been done (Weiss, 1960), is identical with the isomer with melting point 153°, $S_6(NH)_2$ II in Tavs's notation. Direct identification of this compound was not possible as in the publication by Weiss its melting point was not well defined. For isomer $S_6(NH)_2$ I (m.p. 123°C) three-dimensional data were collected. The structure of $S_6(NH)_2$ III (m.p. 130°C) could be found by a comparison of the infrared and mass spectra of the three isomers.

Experimental

Crystal data

Samples of the three isomers were kindly provided by Dr P. Tavs. For all the compounds, suitable crystals could be obtained by recrystallization from benzene solution. When exposed to X-rays or daylight the colourless crystals of isomers I and III turn to yellow. For isomer I it has been observed that the change in colour is accompanied by a decrease in reflecting power. Isomer II appeared to be stable.

The crystallographic data are listed in Table 1. The cell dimensions were obtained from zero layer Weissenberg photographs. For $S_6(NH)_2$ I the photographs were superposed by sodium chloride spots for calibration purposes. The value of the monoclinic angle was determined by measuring $\varphi(100)$ and $\varphi(001)$ on a single-crystal Nonius diffractometer.

Intensity measurements

The intensities for the three-dimensional study of $S_6(NH)_2$ I were measured with an automatic Nonius diffractometer. A crystal of irregular shape was mounted in a Hanff capillary, the monoclinic axis being parallel to the φ axis of the diffractometer. Some details of the intensity measurements are given in Table 2. For 1439 independent reflexions non zero in-

tensity was obtained. Every four hours the intensity of a reference reflexion ($\bar{2},1,4$ or $\bar{2},5,3$) was measured three times. By means of these intensities corrections could be made for the decrease in reflecting power and for changes in the intensity of the primary beam. Corrections for absorption were calculated with a program written according to the Busing & Levy (1957) scheme, the crystal being divided into $8 \times 8 \times 8$ volume elements.

Table 2. Intensity measurement data for the Nonius diffractometer

Radiation:	Mo $K\alpha$; Zr filter.
Method:	$\theta - 2\theta$ scan.
Counter:	Scintillation counter.
Counter slit:	2.4°
Scanning angle:	1.3–1.4°
Scanning speed:	1.2° min ⁻¹ .
θ range:	0–26°.

For $S_6(NH)_2$ II a crystal of dimensions 0.10 × 0.10 × 0.15 mm was mounted along $[\bar{1}01]$ in a capillary. With nickel filtered copper radiation 51 independent reflexions hkh with non zero intensity were collected on an integrated zero layer Weissenberg photograph (Wiebenga & Smits, 1950). The intensities were measured with a densitometer (Smits & Wiebenga, 1953). No corrections for absorption ($\mu R \approx 0.1$) were applied.

Infrared and mass spectra

The infrared spectra were recorded by a Hitachi spectrophotometer (model EPI-G). The samples used were dissolved either in benzene or in KCl pellets. The mass spectra were kindly recorded by Drs P. J. van der Haak and Dr H. J. Hofman (Municipal University of Amsterdam, The Netherlands) by means of an A.E.I.-MS2H mass spectrometer. For $S_6(NH)_2$ III the mass spectrum was obtained at a temperature of 120°C, the other two isomers were analysed at 100°C.

Determination of the structures

Isomer $S_6(NH)_2$ I

The centrosymmetric space group $P2/n$ was adopted as the correct one. This choice was subsequently supported by the results of the structure refinement. Except for the positions of the hydrogen atoms the approximate structure could be found from a three-dimensional Patterson synthesis, calculated with all observed reflexions. To explain all the vectors in this synthesis it was necessary to assume that the asymmetric unit contains two independent molecules. In space

Table 1. Crystal data for the isomers $S_6(NH)_2$

Estimated standard deviations are given in units of the last decimal position, in parentheses.

	Space group	a	b	c	β	D_m	D_x	Z
$S_6(NH)_2$ I (m.p. 130°C)	$Pn, P2/n$	8.054 (3) Å	12.522 (6) Å	8.368 (3) Å	114.45 (5)°	2.00 g.cm ⁻³	1.93 g.cm ⁻³	4
$S_6(NH)_2$ II (m.p. 153°C)	$Pnma$	7.87 (2)	12.86 (3)	7.38 (2)	90	1.98	1.99	4
$S_6(NH)_2$ III (m.p. 123°C)	$Pbca$	8.18 (2)	12.84 (3)	14.06 (3)	90	2.02	2.01	8

group $P2/n$ these molecules lie on twofold special positions *viz.* the twofold axes in the \mathbf{b} direction. Preliminary refinement by means of a three-dimensional difference Fourier synthesis led to an index $R=0.18$. The anisotropic least-squares refinement of the sulphur and nitrogen atoms was carried out according to the block diagonal approximation (Cruickshank, 1961). The 189 weakest reflexions were not considered during the refinement. The least-squares analysis was carried out with a uniform weight for all reflexions until an R value of 0.054 was obtained. A three-dimensional difference map, calculated at this stage of the refinement, indicated that the hydrogen atoms lie in the planes SNS. No accurate parameters could be obtained however. Therefore the coordinates of the hydrogen atoms were calculated with the assumption that the N-H bond has a length of 0.99 Å (Worsham, Levy & Peterson, 1957) and bisects the angle S-N-S. For each of the hydrogen atoms an isotropic temperature factor coefficient was taken to be equal to the mean of the anisotropic temperature parameters U_{ii} of its neighbouring nitrogen atom.

In the final cycles of the least-squares refinement the hydrogen atoms were taken into account with fixed parameters. In addition to the 189 reflexions mentioned above, 6 reflexions of unreliable intensity were omitted. The 195 reflexions are marked with an asterisk in Table 5. For the remaining 1244 reflexions with non-zero intensity the weighting scheme

$$w = [1 + \{(|F(\text{obs})| - 12)/14\}^2]^{-1}$$

was used. After the refinement the value of $w|\Delta F|^2$ appeared to be independent of $|F(\text{obs})|$. The atomic scat-

tering factors taken for sulphur and nitrogen were those of Moore (1963), for the hydrogen atoms the f curve of Stewart, Davidson & Simpson (1965) was used. The index R dropped to 0.048.

The final atomic parameters are listed in Tables 3 and 4. In Table 5 the observed and calculated structure factors are compared. As an analysis of the thermal parameters showed that the molecules cannot be considered as rigid bodies vibrating about their centres of mass, the coordinates were not corrected for libration effects.

Isomer $S_6(\text{NH})_2$ II

The crystal data indicated that isomer $S_6(\text{NH})_2$ II is identical with the compound $S_6(\text{NH})_2$ previously investigated by Weiss (1960). The identity of the two compounds was established by a study of the $[\bar{1}01]$ projection of isomer II. A structure factor calculation for 51 reflexions hkh , based on Weiss's coordinates and an overall isotropic temperature factor $\exp(-2.5 \sin^2 \theta/\lambda^2)$ gave $R=0.12$.

In agreement with Weiss's results an $F(\text{obs})$ electron density map of the $[\bar{1}01]$ projection clearly showed that in isomer $S_6(\text{NH})_2$ II the nitrogen atoms are in 1,5 positions in an eight-membered ring of sulphur and nitrogen atoms.

Isomer $S_6(\text{NH})_2$ III

As pointed out in the introduction only the structures (a) to (c) are expected for the isomers $S_6(\text{NH})_2$. Structure (d) could also be excluded by considering the infrared and mass spectra of the three compounds. None of the infrared spectra show vibrations corre-

Table 3. Fractional atomic coordinates with standard deviations, in parentheses, in units of the last decimal position as calculated by the least-squares program

Molecule A				Molecule B			
	x	y	z		x	y	z
N(1)	-0.0067 (5)	-0.0602 (3)	0.2390 (5)	N(2)	0.2402 (6)	0.5266 (4)	0.5048 (5)
S(1)	0.1747 (2)	-0.1497 (1)	0.3234 (2)	S(4)	0.3278 (2)	0.6148 (1)	0.6786 (3)
S(2)	0.0155 (2)	0.0647 (1)	0.3224 (2)	S(5)	0.3350 (2)	0.3999 (1)	0.5314 (2)
S(3)	0.1107 (2)	0.1643 (1)	0.1869 (2)	S(6)	0.1890 (2)	0.2994 (1)	0.6151 (2)
H(1)	-0.12	-0.08	0.14	H(2)	0.14	0.55	0.39

Table 4. Thermal parameters U_{ij} (10^{-4} Å²) of the temperature factor $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^*)]$

Standard deviations are given in parentheses.

Molecule A						
	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
N(1)	441 (22)	526 (24)	474 (22)	-345 (36)	-268 (36)	491 (37)
S(1)	579 (8)	490 (8)	580 (8)	-171 (12)	208 (12)	410 (13)
S(2)	502 (7)	689 (9)	505 (7)	-81 (12)	-156 (13)	668 (12)
S(3)	441 (6)	465 (7)	455 (6)	149 (10)	66 (10)	365 (10)
Molecule B						
	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
N(2)	540 (25)	632 (28)	464 (23)	-357 (43)	340 (40)	328 (39)
S(4)	635 (9)	499 (9)	952 (12)	-409 (14)	362 (16)	143 (17)
S(5)	631 (9)	816 (11)	648 (8)	-169 (15)	-131 (15)	862 (15)
S(6)	557 (7)	458 (7)	534 (7)	-174 (11)	-168 (11)	422 (12)

Table 5 (cont.)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC					
-4	6	6	95	-91	6	10	1	24	-1*	-9	10	5	21	10*	3	11	1	54	-6C	-5	11	5	36	-56*	-2	17	2	17	3*	0	13	0	374	404	0	13	5	66	64
-3	9	8	193	150	-7	10	2	116	-119	-9	10	5	202	208	4	11	1	99	-103	-4	11	5	73	-74	-1	17	7	65	-69	1	13	0	33	-54	1	14	0	34	-23
-2	6	8	96	62	-4	10	2	231	233	-4	10	5	29	-35*	5	11	1	9	22*	-3	11	7	37	-9*	3	17	7	62	-98	2	13	0	106	-110	2	14	0	28	35*
-1	6	6	160	-164	-4	10	2	160	-169	-3	10	5	166	-166	-6	11	2	26	-42*	-2	11	5	183	-170	1	17	7	144	141	3	13	0	48	-59	3	14	0	54	-52
0	6	6	232	-217	-3	10	2	107	-102	-2	10	5	82	-83	-9	11	2	248	-248	-1	11	5	53	-51	2	17	7	69	-67	4	13	0	88	-84	-4	14	1	121	120
1	6	6	21	-18*	-2	10	2	33	36	-1	10	5	225	209	-4	11	2	20	31*	0	11	5	30	-30	3	17	7	191	-184	-9	13	1	98	-94*	-3	14	1	102	97
-6	5	7	114	117	-1	10	2	38	40	0	10	5	112	-103	-3	11	2	126	120	1	11	4	24	-29*	4	17	7	11	-79*	-4	13	1	62	61	-2	14	1	15	-53
-9	6	7	74	-74	0	10	2	298	304	-9	10	5	94	-99	-2	11	2	182	183	-4	11	6	17	-10*	-5	17	7	25	-25	0	13	1	78	88	-1	14	1	6	-4*
-3	6	7	98	-50	1	10	2	15	-16*	0	10	5	17	-18*	1	11	2	32	30	-3	11	6	215	-199	-9	17	7	127	145	-2	13	1	106	102	1	14	1	123	-126
-2	6	7	3	-18*	2	10	2	44	-42	3	10	5	119	-110	1	11	2	124	-127	-2	11	6	94	-97	-4	17	7	49	51	-1	13	1	13	-21*	2	14	1	7	-12*
-1	6	7	34	-12*	3	10	2	166	-166*	-9	10	6	38	-10	2	11	2	11	-28*	7	11	6	59	-24	-3	17	7	47	-53	0	13	1	115	-110	3	14	1	96	92
0	6	7	104	102*	4	10	2	101	95	-4	10	6	80	87	3	11	2	85	-91	1	11	6	107	101	-1	17	7	45	-48	3	13	1	48	-43	-4	14	2	76	-73
1	6	7	73	76	5	10	2	14	-43*	-3	10	6	176	-196	4	11	2	38	41	-4	11	7	32	34*	0	17	7	61	-56	4	13	1	120	113	-3	14	2	35	-46
-9	8	10	107	-70	-7	10	3	157	-148	-2	10	6	120	-110	5	11	2	90	-89	-3	11	7	63	66	1	17	7	91	-76	-9	13	2	72	69	-2	14	2	30	-2*
-4	8	10	102	-99	-8	10	3	100	-102	0	10	6	104	-112	-6	11	3	67	73	-2	11	7	152	157	2	17	7	62	-64	-4	13	2	92	91	-1	14	2	75	-80
-2	6	8	89	76	-4	10	3	126	124	1	10	6	36	29	-9	11	3	112	-129	1	12	0	35	-24	3	17	7	93	90	-3	13	2	80	-84	0	14	2	95	-59
-1	6	8	95	-96	-3	10	3	16	16*	-5	10	7	77	78	-3	11	3	107	122	3	12	0	34	30	-5	17	7	75	79	-1	13	2	86	-84	-3	14	3	75	-73
1	10	0	46	-97	-1	10	3	168	-141	-3	10	7	83	-78	-2	11	3	298	219	4	12	0	71	-68	-4	17	7	104	104	-4	13	2	110	-136	-7	14	2	142	-144
2	10	0	210	-233	0	10	3	69	-67	-2	10	6	100	94	-1	11	3	102	-104	5	12	0	67	65	-3	17	7	105	105	3	13	2	111	-110	-1	14	3	98	104
3	10	0	161	183	1	10	3	76	83	-1	10	7	34	-32*	0	11	3	132	135	-6	12	1	27	-28*	-6	17	7	176	-185	-2	13	2	117	11*	0	14	3	87	91
4	10	0	97	-99	3	10	3	66	-95	0	10	7	119	118	1	11	3	137	-142	-9	12	1	93	-87	-1	17	7	40	-28	3	13	2	52	-64	-1	14	3	83	84
5	10	0	0	0*	4	10	3	34	-32	C	11	0	192	-187	1	11	3	162	-164	-4	12	1	37	-29*	3	17	7	47	87	-5	13	3	111	89	-1	14	4	35	-38
6	10	0	63	58	5	10	3	77	-72	1	11	0	23	-26*	3	11	3	117	121	-3	12	1	46	-55	1	17	7	31	-12	-4	13	3	62	-64	-2	14	4	75	82
-7	10	1	8	-16*	-7	10	4	38	35	3	11	0	143	-155	4	11	3	156	-155	-2	12	1	82	-90	2	17	7	42	33	-2	13	3	39	38	-1	14	4	35	-28
-6	10	1	113	114	-6	10	4	107	-106	4	11	0	29	24	-6	11	4	82	88	0	12	1	206	203	-1	17	7	123	-110	-1	13	3	93	-82	2	15	0	95	-80
-9	10	1	203	197	-9	10	4	107	104	9	11	0	29	24	-9	11	4	95	102	0	12	1	24	-25*	-4	17	7	61	62	-1	13	3	80	77	2	15	0	94	70
-8	10	1	124	-120	-4	10	4	60	60	8	11	0	90	-103	-4	11	4	17	-19*	1	12	1	182	-174	-3	17	7	47	42	2	13	3	64	71	-2	15	1	26	-31*
-3	10	1	115	-119	-3	10	4	194	198	-6	11	1	107	-106	-3	11	4	191	192	2	12	1	112	111	-2	17	7	134	-138	-4	13	4	108	-114	-1	15	1	91	-92*
-2	10	1	8	9*	-2	10	4	92	47	-9	11	1	24	-20*	-2	11	4	110	-102	3	12	1	73	-84	-1	17	7	64	-68	-2	13	4	99	110	0	15	1	91	97
-1	10	1	316	-312	-1	10	4	67	-67	-1	11	1	116	116	-1	11	4	98	-78	4	12	1	15	6*	0	17	7	72	-71	-1	13	4	150	150	1	15	1	12	4*
0	10	1	286	296	1	10	4	83	-98	-3	11	1	95	03	0	11	4	93	94	5	12	1	91	44	1	17	7	65	51	0	13	4	88	-86	-2	15	2	171	-175
1	10	1	427	-417	2	10	4	65	-67	-2	11	1	17	-19*	1	11	4	77	-80	-6	12	2	48	-36	-4	17	7	66	-62	1	13	4	10	30*	-1	15	2	49	-45
2	10	1	16	27*	3	10	4	195	171	0	11	1	9	9	0	11	4	93	44	-5	12	2	157	160	3	17	7	31	-32*	-4	13	4	92	-88	-2	15	2	47	-43
4	10	1	42	-42	4	10	4	93	-97	1	11	1	39	37	3	11	4	24	16*	-4	12	2	131	-121	-2	17	7	66	44	-3	13	4	91	-90	0	15	2	48	-40*
5	10	1	86	-88	-7	10	9	75	87	2	11	1	243	258	-6	11	5	113	114	-3	12	2	223	-219	-1	17	7	68	54	-2	13	4	43	-45					

Table 6. Intramolecular distances and angles with e.s.d.'s, in units of the last decimal position, in parentheses

For the numbering of the atoms see Fig. 2.

Molecule A

N(1)—S(1)	1.742 (10) Å	S(1)—N(1)—S(2)	120.0 (5)°
N(1)—S(2)	1.691 (10)	N(1)—S(1)—S(1')	111.2 (4)
S(1)—S(1')	2.053 (6)	N(1)—S(2)—S(3)	109.6 (4)
S(2)—S(3)	2.037 (4)	S(2)—S(3)—S(3')	107.3 (2)
S(3)—S(3')	2.047 (6)		
N(1)···S(1')	3.136 (10)		
N(1)···S(3)	3.054 (10)		
S(1)···S(2)	2.973 (4)		
S(2)···S(3')	3.290 (4)		

Molecule B

N(2)—S(4)	1.727 (10) Å	S(4)—N(2)—S(5)	118.2 (5)°
N(2)—S(5)	1.735 (10)	N(2)—S(4)—S(4')	110.8 (4)
S(4)—S(4')	2.059 (8)	N(2)—S(5)—S(6)	108.9 (4)
S(5)—S(6)	2.034 (5)	S(5)—S(6)—S(6')	107.3 (2)
S(6)—S(6')	2.056 (6)		
N(2)···S(4')	3.121 (10)		
N(2)···S(6)	3.071 (10)		
S(4)···S(5)	2.970 (6)		
S(5)···S(6')	3.294 (5)		

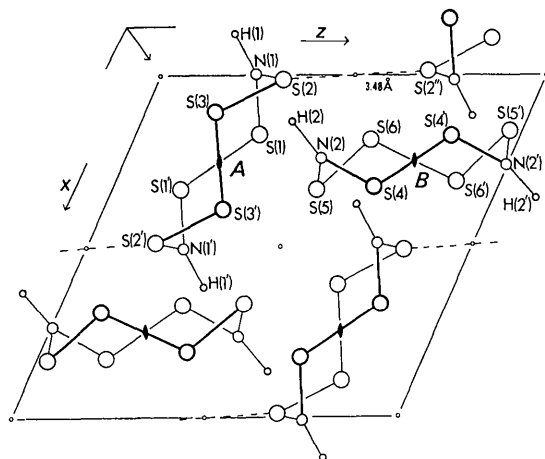


Fig. 2. Projection of the structure of S₆(NH)₂ I along the monoclinic axis.

sponding with a N–N-group, whereas in the mass spectra in all cases, only a negligibly small amount of N₂H₂ was detected. In view of the structures (b) and (c) found for I and II respectively, this leaves structure (a) for isomer III. This compound is thus cyclohexasulphur-1,3-diimide.

In agreement with the difference Fourier synthesis of S₆(NH)₂ I the infrared spectra of I shows that the hydrogen atoms are linked to the nitrogen atoms. For the isomers S₆(NH)₂, N–H stretch vibrations (3400–3200 cm⁻¹) were observed as well as bands corresponding to N–S stretch vibrations (850–750 cm⁻¹).

Discussion of the structure of S₆(NH)₂ I

Molecular structure

In Fig. 2 the structure of S₆(NH)₂ I projected on to (010) is given. Intramolecular distances and angles are

listed in Table 6. The estimated standard deviations in this Table were calculated from those in Table 3 after multiplication by a factor of two.

Both independent molecules, *A* and *B* in Fig. 2, have the crown conformation. The ring atoms of a molecule may be divided into two groups, forming two parallel planes to a fairly good approximation (Table 7). For molecule *A* as well as for *B* these planes intersect the *x, z* plane at an angle of about 88° .

Table 7. Distances to the 'best' plane through N(1), S(3), S(1'), S(2') (above) and to the best plane through N(2), S(6), S(4') and S(5') (below)

The planes obey the equation $0.5035X + 0.0275Y + 0.8636Z = 1.5967$ and $0.9922X - 0.0261Y + 0.1220Z = 1.9087$ respectively, with $X = x \sin \beta$, $Y = y$ and $Z = z + x \cos \beta$ (in Å).

N(1)	0.1045 Å	N(1')	0.6801 Å
S(3)	-0.0994	S(3')	1.0388
S(1')	-0.1075	S(1)	0.8304
S(2')	0.1024	S(2)	0.7682
N(2)	0.0847 Å	N(2')	0.7200 Å
S(6)	-0.0801	S(6')	1.0329
S(4')	-0.0877	S(4)	0.8348
S(5')	0.0831	S(5)	0.8043

A molecule $S_6(NH)_2$ I and its mirror image are not superimposable (Fig. 3). As both optical configurations are present in the unit cell the crystals are racemates.

Fig. 4 shows the molecules schematically, with bond lengths and angles. The values of the bond angles are characteristic for sp^2 hybridization at the nitrogen atoms and sp^3 hybridization at the sulphur atoms. Except for the distance N(1)–S(2) (1.69 Å) all N–S bond lengths are only slightly shorter than the length of a 'single' N–S bond in H_3NSO_3 (1.76 Å; Sass, 1960). They are larger, however, than the N–S bonds in $S_4(NH)_4$, 1.67 Å on average (Sass & Donohue, 1958), indicating a larger double bond character for the N–S bonds in the latter compound. In agreement with this the angles S–N–S in $S_4(NH)_4$ (average value 122.2°) are larger than those in $S_6(NH)_2$ I (average value 119.1°).

The S–S distances (average value 2.048 Å) agree very well with those in orthorhombic sulphur (average value 2.048 Å; Cooper, Bond & Abrahams, 1961; 2.047 Å, Caron & Donohue, 1965). They are shorter than the lengths of the outer S–S bonds in the ions $[O_3S-(S)_x-SO_3]^{2-}$ (Table 8). This may be explained by the fact that the SO_3 groups have no lone pairs available for the formation of $d_\pi-d_\pi$ bonds, which occurs to a small extent in $S_6(NH)_2$ I and in S_8 .

Arrangement of the molecules

The structure consists of alternating layers of molecules *A* and *B*, lying on the glide planes $y=0$ and $y=\frac{1}{2}$ respectively (Fig. 5). The shortest intermolecular distances are about equal to the sum of the van der Waals radii (Pauling, 1960), except for the distance $S(2) \cdots S(2')$, which is about 0.22 Å shorter. It is remarkable that the sulphur atoms, which form the short $S \cdots S$ contact, are also involved in the short N–S bond of 1.69 Å. Although it is probable that the shortening



Fig. 3. The two optical configurations of $S_6(NH)_2$ I.

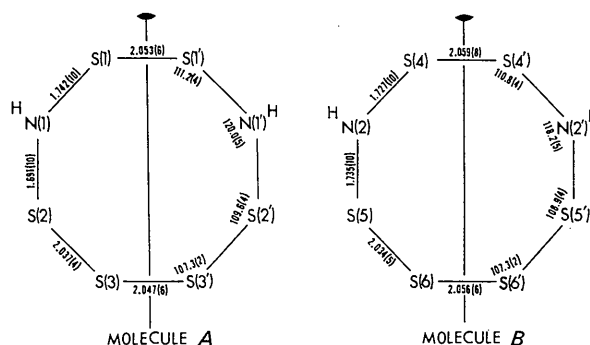


Fig. 4. Bond lengths and angles in $S_6(NH)_2$ I. The e.s.d.'s, in units of the last decimal position, are given in parentheses.

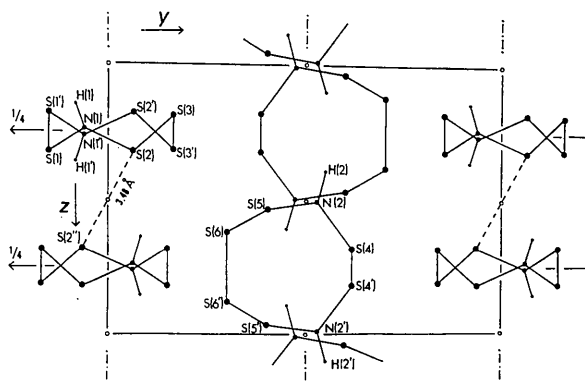


Fig. 5. Projection of the structure of $S_6(NH)_2$ I along [100] on to the plane (100).

Table 8. Sulphur–sulphur distances (in Å) in the ions $[O_3S-(S)_x-SO_3]^{2-}$

	S–S (end)	S–S in $(S)_x$	Reference
$K_2S_2O_6$	2.15	—	Stanley, 1956.
$BaS_4O_6 \cdot 2H_2O$	2.12	2.02	Foss, Furberg & Zachariasen, 1954.
$Na_2S_4O_6 \cdot 2H_2O$	2.12	2.02	Foss & Hordvik, 1964.
$K_2Ba(S_6O_6)_2$	2.10	2.04	Foss & Johnsen, 1965.
$(CoCl_2en)_2S_6O_6 \cdot H_2O$	2.12	2.04	Foss & Marøy, 1965.

is due to strong intermolecular interaction, an explanation could not be given for this effect. The stronger interaction of the molecules *A* in comparison with *B* is also reflected by the relatively small thermal motion of *A* (Table 4).

Calculations were done at the Groningen University Computing Centre. We thank Professor E. H. Wiebenga and Professor F. Jellinek for their interest during the course of this investigation. We are indebted to Drs R. Olthof-Hazekamp for programming the calculations, and to Drs J. L. de Boer and Mr F. van Bolhuis for their assistance during the experimental work.

References

- BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.
 CARON, A. & DONOHUE, J. (1965). *Acta Cryst.* **18**, 562.
 COOPER, A. S., BOND, W. L. & ABRAHAMS, S. C. (1961). *Acta Cryst.* **14**, 1008.
 CRUICKSHANK, D. W. J. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. London: Pergamon Press.
 FOSS, O., FURBERG, S. & ZACHARIASEN, H. (1954). *Acta Chem. Scand.* **8**, 459.
 FOSS, O. & HORDVIK, A. (1964). *Acta Chem. Scand.* **18**, 662.
 FOSS, O. & JOHNSEN, K. (1965). *Acta Chem. Scand.* **19**, 2207.
 FOSS, O. & MARØY, K. (1965). *Acta Chem. Scand.* **19**, 2219.
 GOEHRING, M., HERB, H. & KOCH, W. (1951). *Z. anorg. Chem.* **264**, 137.
 HEAL, H. G. (1963). *Nature, Lond.* **199**, 371.
 HEAL, H. G. & KANE, J. (1964). *Nature, Lond.* **203**, 971.
 LUND, E. W. & SVENDSEN, S. R. (1957). *Acta Chem. Scand.* **11**, 940.
 MEUWSEN, A. & LÖSEL, M. (1953). *Z. anorg. Chem.* **271**, 217.
 MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169.
 PAULING, L. (1960). *The Nature of the Chemical Bond*. 3rd ed. Ithaca, New York: Cornell Univ. Press.
 SASS, R. L. (1960). *Acta Cryst.* **13**, 320.
 SASS, R. L. & DONOHUE, J. (1958). *Acta Cryst.* **11**, 497.
 SMITS, D. W. & WIEBENGA, E. H. (1953). *J. Sci. Instrum.* **30**, 280.
 STANLEY, E. (1956). *Acta Cryst.* **9**, 897.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
 TAVS, P., SCHULZE-STEINEN, H. J. & COLCHESTER, J. E. (1963). *J. Chem. Soc.* p. 2555.
 WEISS, J. (1959). *Z. angew. Chem.* **71**, 246.
 WEISS, J. (1960). *Z. anorg. Chem.* **305**, 190.
 WEISS, J. & NEUBERT, H. S. (1965). *Acta Cryst.* **18**, 815.
 WIEBENGA, E. H. & SMITS, D. W. (1950). *Acta Cryst.* **3**, 265.
 WORSHAM, J. E., LEVY, H. A. & PETERSON, S. W. (1957). *Acta Cryst.* **10**, 319.

Acta Cryst. (1969). **B25**, 617

Structures Cristallines du Diphényl-thio-phosphinite de Méthyle et du Diphényl-sélénio-phosphinite de Méthyle

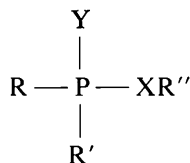
PAR G. LEPICARD, D. DE SAINT-GINIEZ-LIEBIG, A. LAURENT ET C. RERAT
Laboratoire de Cristallographie, C.N.R.S., Bellevue, Hauts de Seine, France

(Reçu le 13 mars 1968)

The crystals of methyl diphenyl-thiophosphinite, $(C_6H_5)_2P(S)OCH_3$, and methyl diphenyl-selenophosphinite, $(C_6H_5)_2P(Se)OCH_3$, are isomorphous. The two compounds are monoclinic, space group $P2_1/a$, with four molecules in a unit cell of dimensions: $a=11.78$, $b=12.62$, $c=9.42$ Å; $\beta=112^\circ$ for the thio compound, and $a=11.73$, $b=12.86$, $c=9.42$ Å; $\beta=113^\circ$ for the seleno compound. The crystal structures were determined from three-dimensional X-ray data at room temperature using Patterson and Fourier methods, and refined by the least-squares method. The final *R* value is 0.153 for the thio and 0.144 for the seleno compound. The phosphorus is tetrahedrally connected with two phenyl groups ($P-C=1.81$ Å, mean value), one oxygen ($P-O=1.60$ Å) and sulphur ($P-S=1.94$ Å) or selenium ($P-Se=2.09$ Å).

Introduction

L'étude par diffraction des rayons X des structures de $(C_6H_5)_2P(S)OCH_3$ et $(C_6H_5)_2P(Se)OCH_3$ constitue une participation à l'étude des composés organo-phosphorés de formule générale:



dans laquelle R, R' et R'' sont des groupes alcoyle ou aryle, X=O, S, et Y=O, S, Se.

La réactivité des composés étudiés dépend de la nature des atomes ou radicaux liés au phosphore (Nguyen-Thanh, Clergue, Larruat & Chabrier, 1964) et on peut penser que ces différences de réactivité peuvent s'expliquer par des différences de structure moléculaire.

Les diphényl-thio(et sélénio)-phosphinites de méthyle ont été préparés au laboratoire de M. Chabrier, à la Faculté de Médecine de Paris, en faisant agir le méthanol sur le chlorodiphénylphosphinite en solution pyri-