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Thiosinamine의 결정 및 분자구조

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The Crystal and Molecular Structure of Thiosinamine

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요 약. Thiosinamine, $H_2NCSNHCH_2CH\ CH_2$의 결정 및 분자구조를 X-선 회절법으로 규명하였다. 이 결정은 공간군 $P2_1/a$의 단사정계에 속하며 단위세포상수는 $a=9.819(3)$, $b=8.553(3)$, $c=9.170(2)$Å, $\beta=127.3(1)°$이고 $z=4$이다. 814개의 회절 반점에 대한 강도 data는 Regaku-Denki 자동 4축 회절기를 써서 얻었다. 구조는 직접법과 Fourier법으로 규명하였으며 좌표의 정밀화는 Full Matrix 최소 자승법에 의하여 행하였고 최종의 R값은 0.046이다. Thiourea moiety는 평면이며, 결합길이와 결합각은 thiourea unit를 포함하는 화합물에서 얻어진 값들과 잘 일치하고 있다. 분자들은 결정내에서 b축을 따라 두 종류의 N−H···S 수소결합에 의하여 상호 결합하고 있다.

ABSTRACT. The crystal and molecular structure of thiosinamine, $H_2NCSNHCH_2CHCH_2$, has been determined by X-ray diffraction method. The crystals are monoclinic, space group $P2_1/a$ with four molecules in a unit cell of dimensions, $a=9.819(3)$, $b=8.553(3)$, $c=9.170(2)$Å, $\beta=127.3(1)°$, and $z=4$. Intensity data for 814 reflections were collected with a Rigaku-Denki automatic four circle diffractometer. The structure was solved by direct and Fourier methods. Refinements were carried out by full matrix least-squares method to a final R value of 0.046. The thiourea unit is planar, and the bond lengths and angles in that unit agree well with those in the compounds which contain a thiourea moiety. The molecules are linked together by the two patterns of N−H···S hydrogen bonds along the b-axis.

INTRODUCTION

We have determined the crystal structure of thiosinamine by X-ray diffraction methods. Numerous crystal structures of the compounds containing a thiourea moiety which are related to thiosinamine have been determined previously. In this paper, the molecular conformation and hydrogen bonding scheme in the thiosinamine crystals are discussed and the structure of thiosinamine are compared with those of other thiourea derivatives.

EXPERIMENTAL

White, pyramidal crystal of thiosinamine were grown from an absolute ethanol solution. Oscillation and Weissenberg photographs showed the monoclinic symmetry of the crystals and

yielded approximate lattice constants. These cell parameters were refined by the least-squares method using 30 reflections ($15°<2\theta<40°$) measured on the Rigaku-Denki automatic four-circle diffractometer with MoK_α radiation. The systematic absences of hOl when $h=2n+1$ and OKO when $k=2n+1$ indicated that the space group was $P2_1/a$.

The density was measured by flotation method in a mixture of benzene and chloroform.

Crystal data of thiosinamine

$C_4H_8N_2S$	mp 78°C
Monoclinic	space group ; $P2_1/a$
M. W. ; 116. 19	Z ; 4
a ; 9. 819(3) Å	$F(000)$; 248. 0
b ; 8. 553(3) Å	V ; 612. 5Å^3
c ; 9. 170(2) Å	Dc ; 1. 26gcm^{-3}
β ; 127. 3(1)°	Dm ; 1. 22gcm^{-3}
μ ; 3. 57mm^{-1}	

A crystal with approximate dimensions of 0. 3×0. 3×0. 3mm was selected for the data collection. The intensities of 1528 unique reflections with $0°<2\theta<55°$ were measured using a Rigaku-Denki Automatic four circle diffractometer with graphite-monochromatized Mo-K_α radiation in the ω-2θ scan mode, with a scan speed of 4° min^{-1} in 2θ and a scan width of $(1.2+0.5\tan\theta)°$ in ω. At both ends of the scan range 10 seconds background counts were taken for each reflection. Three reference reflections were monitored after every 50 reflections and showed only small random deviations from their mean intensities. 814 independent reflections were considered observed ($F_0>6\sigma(F_0)$) and were included in the subsquent calculations. The intensity data were reduced to structure factors by the application of Lorentz and polarization factors, and no absorption corrections were applied.

STRUCTURE DETERMINATION AND REFINEMENT

Preliminary Phases for the structure factors were derived by the direct method using the program system MULTAN[1]. The known geometry of the molecular fragment (4 atoms of the thiourea moiety) was used to modify the Wilson plot[2]. 70 reflections having $|E|$ values greater than 1. 60 were used.

The phase set with the largest combined figure of merit was selected, and the subsequent $|E|$ map calculated with these phases revealed the positions of the 4 atoms of the thiourea moiety. The subsequent structure factor calculation and Fourier synthesis gave the positions of the remaining non-hydrogen atoms. Structure factor calculation based on all non-hydrogen atoms with 814 reflections gave the initial R value of 0. 18.

Refinements were performed by the full matrix least-squares method using the SHELX 76[3] program system. Two cycles of refinement using anisotropic temperature factors resulted in the R value of 0. 069.

A difference Fourier synthesis was then calculated and the positions of the eight hydrogen atoms could be located. In the final cycle, the positional and anisotropic thermal parameters

Table 1. Fractional atomic coordinates for the non-hydrogen atoms in thiosinamine. The e. s. d's are given in parentheses and refer to the last decimal positions

Atom	X/a	Y/b	Z/c
S	0. 6800(1)	0. 0596(1)	−0. 0511(2)
N(1)	0. 9828(5)	−0. 0732(5)	0. 1666(6)
N(2)	0. 9837(5)	0. 1922(4)	0. 1693(5)
C(1)	0. 8954(5)	0. 0598(5)	0. 1043(6)
C(2)	1. 1694(6)	0. 2032(6)	0. 2925(6)
C(3)	1. 2535(7)	0. 1675(6)	0. 4888(7)
C(4)	1. 1846(9)	0. 1444(8)	0. 5720(9)

Table 2. Anisotropic thermal parameters U_{ij} ($\times 10^3$) for the non-hydrogen atoms in thiosinamine, together with their e. s. d's. The U_{ij} values given are defined by the temperature factor ; exp $[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2C^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	35.5(0.5)	24.4(0.4)	53.5(0.7)	−3.4(0.6)	14.8(0.5)	2.5(0.6)
N(1)	37(2)	21(2)	51(2)	−1(2)	17(2)	0(2)
N(2)	43(2)	20(2)	44(2)	0(2)	20(2)	0(2)
C(1)	42(2)	22(2)	31(2)	1(2)	22(2)	2(2)
C(2)	47(3)	36(2)	43(3)	−3(2)	23(2)	−10(2)
C(3)	47(2)	49(3)	47(3)	−10(2)	24(2)	−9(2)
C(4)	83(4)	62(4)	66(4)	−4(3)	47(4)	−13(3)

Table 3. Fractional atomic coordinates and isotropic thermal parameters $U(\times 10^2)$ for the hydrogen atoms in thiosinamine. The e. s. d's are given in parentheses.

Atom	*X/a*	*Y/b*	*Z/c*	*U*
H(1)	1.092(6)	−0.071(5)	0.241(6)	5(1)
H(2)	0.936(6)	−0.138(5)	0.133(7)	4(2)
H(3)	0.933(5)	0.260(5)	0.122(6)	6(2)
H(4)	1.208(5)	0.303(5)	0.278(6)	5(1)
H(5)	1,212(5)	0.135(5)	0.238(6)	6(2)
H(6)	1.381(5)	0.147(5)	0.565(6)	9(2)
H(7)	1.056(6)	0.150(5)	0.505(6)	11(2)
H(8)	1.165(6)	0.212(5)	0.524(7)	3(2)

for the non-hydrogen atoms and the positional and isotropic thermal parameters for the hydrogen atoms were refined. The final R value was reduced to 0.046.

The fractional coordinates and thermal parameters are listed in Table 1∼3, together with their estimated standard deviations.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Molecular Conformation, Interatomic bond lengths and angles with their standard deviations are given in *Fig.* 1.

The C(1)—S bond length of 1.688Å agrees well with the C—S bond lengths in other related compounds (*Table* 4). In all the cases the C—S bond lengths are intermediate between the C—S single bond length of 1.82Å and the C—S double bond length of 1.56Å quoted by Sutton[4]. Therefore, the C—S bond in this compound posseses a partial double bond character in agreement with the following resonance forms;

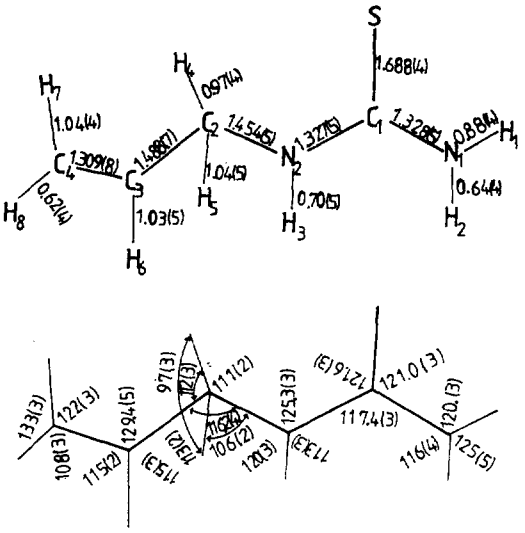

Fig. 1. Bond lengths(Å) and angles(°) with labelling scheme of atoms.

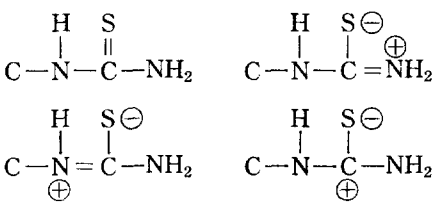

Table 4. C-S bond lengths in related compounds

Compounds	C-S
Thiosinamine	1.688Å
4-Formylpyridine thiosemicarbazone[5]	1.678Å
2-Formyl-4-phenylpyridine thiosemicarbazone[6]	1.675Å
2-Formylthiophene thiosemicarbazone[7]	1.698Å
2-Keto-3-ethoxybutylaldehyde thiosemicarbazone[8]	1.692-1.689Å
thiosemicarbazide[9]	1.685Å
4-phenylthiosemicarbazide[10]	1.685Å
1-phenylthiosemicarbazide[11]	1.696Å
Morpholinothiosemicarbazide[12]	1.69Å
N, N-Dibenzyl-N-diphenoxyphospharylthiourea[13]	1.683Å

Table 5. Equation of least-squares plane and deviations of the atoms from the plane in thiosinamine. Equation for plane ; $-0.6721X-0.0081Y+0.7420Z=-4.9589$

Atoms in plane	Atom of out of plane	Distances in Å from best plane
S		0.00011
N(1)		0.00017
N(2)		0.00016
C(1)		0.00045
	C(2)	−0.09976

The C(1)—N(1) bond length of 1,328Å and the N(2)—C(1) bond length of 1.327Å are also indicative of some double bond character, in agreement with the resonance forms.

The bond lengths of N(2)—C(2) and C(3)—C(4) are 1.454 and 1.309Å respectively, whereas the normal N—C single bond and C—C double bond length are 1.47 and 1.34Å, respectively. The C(2)—C(3) bond length of 1.488Å is shorter than the normal C—C single bond length of 1.54Å.

The equation of the least-squares plane of a thiourea moiety and the deviations of the various atoms from this plane are given in *Table* 5. The atoms of the thiourea moiety are coplanar within 0.0005Å.

Intermolecular Packing and Hydrogen Bonding. The projections of the structure down the *b*-axis and the *c*-axis are shown in *Fig.* 2 and 3, respectively. There are no intermolecular contacts shorter than the normal Van der Waals distance except two intermolecular hydrogen bonds. The principal hydrogen bond motif involves ribbons of molecules related by the twofold screw axis parallel to the *b*-axis. The two nitrogen atoms act as donors to the sulfur atom, and the N(1)···S and N(2)···S lengths

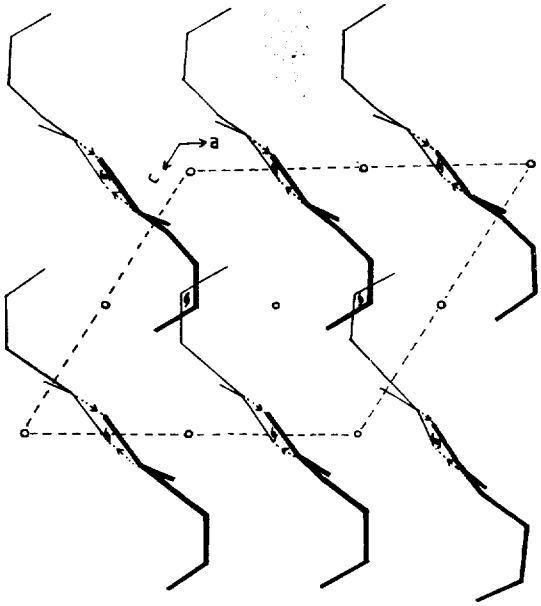

Fig. 2. The crystal structure of thiosinamine viewed down the *b*-axis. Dotted lines are hydrogen bonds. Arrows indicate donor direction

Table 6. Distances and angles for the hydrogen bonds

D	H	A	D···A	H···A	D–H···A
N(1)	H(1)	S(*a*)	3.390Å	2.74Å	166.0°
N(2)	H(3)	S(*b*)	3.394Å	2.71Å	161.3°

S(*a*) at 3/2 $-X$, $-1/2$ $-Y$, $-Z$
S(*b*) at 3/2 $-X$, 1/2 $-Y$, $-Z$

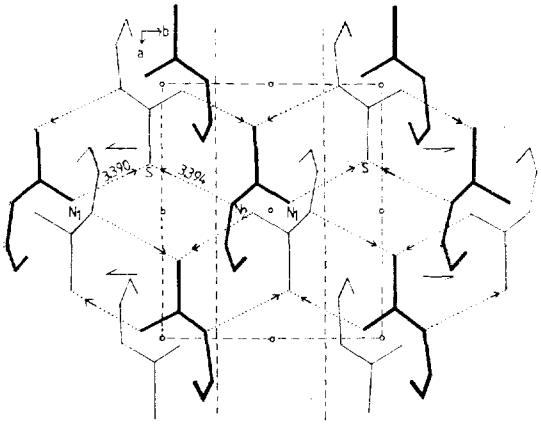

Fig. 3. The crystal structure of thiosiamine viewed down the *c*-asis. Dotter lines are hydrogen bond. Arrows inidicate donor direction.

are 3.390 and 3.394Å, respectively. Details of the hydrogen bonds are given in *Table* 6.

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