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Sulfadiazine의 結晶 및 分子構造

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The Crystal and Molecular Structure of Sulfadiazine

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요 약. X-선 회절법을 이용하여 sulfadiazine, $C_{10}H_{10}N_4O_2S$, 의 결정 및 분자 구조를 규명하였다. Acetone과 ethanol의 혼합용액으로 부터 얻은 결정은 일사축계에 속하며, 단위세포에는 4분자가 있고, 공간군은 $P2_1/c$이다. 단위세포 상수는 $a=13.71\pm0.04$, $b=5.84\pm0.03$, $c=15.11\pm0.05$ Å, $\beta=115.0\pm0.3°$이다. 결정구조는 3차원적인 와이센버그사진으로 부터 얻어진 실험치를 이용하여 패터슨함성과 프리에합성을 하고 이를 해석하여 밝혀냈다. 수소원자를 제외한 원자들의 좌표치는 최소자승법으로 정밀화 하였으며, 최종 R값은 관측된 1517개의 독립반사에 대하여 0.15이다. 벤젠고리와 피리미딘고리의 두 평면이 이루는 각은 76°이고, S—N(1)결합을 중심으로 한 N(1)—C(1)결합과 S—C(5)결합이 이루는 conformational angle은 77°로서 *gauche*형을 하고 있다. 이미노기의 질소원자, N(1)은 대칭중심에 의하여 옮겨지는 다른분자의 피리미딘고리의 질소원자, N(3)와 N—H···N형의 수소결합을 이루고 있으며, 아미노기의 질소원자, N(4)는 b축의 거리만큼 떨어져 있는 다른분자의 산소원자, O(1) 및 O(2)와 두개의 N—H···O형 수소결합을 이루고 있다. 이들 수소결합의 2차원적 그물은 (100)면에 평행한 무한한 분자층을 형성하며 인접분자층 사이에는 van der Waals의 힘에 의하여 결합되어 있다.

Abstract. Sulfadiazine, $C_{10}H_{10}N_4O_2S$, forms monoclinic crystals of space group $P2_1/c$ from a mixture of acetone and ethanol with $a=13.71\pm0.04$, $b=5.84\pm0.03$, $c=15.11\pm0.05$Å, $\beta=115.0\pm0.3°$, and four molecules per cell. Three dimensional photographic data were collected with Cu $K\alpha$ radiation. The structure was determined using Patterson and Fourier synthesis methods and refined by block diagonal least-squares methods with isotropic thermal parameter for all non-hydrogen atoms. The final R value was 0.15 for the 1517 observed independent reflections. The dihedral angle between the planes through the benzene ring and the pyrimidine ring is 76°. The

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conformational angle formed by the projection of the S—C(5) bond with that of N(1)—C(1) whe the projection is taken along the S—N(1) bond is 77°. The imino nitrogen atom, N(1), and pyrimidine nitrogen atom, N(3), form intermolecular N—H···N hydrogen bond between the molecules related by center of symmetry. Amino nitrogen atom, N(4), forms two intermolecular N—H···O hydrogen bonds, with O(1) and O(2) atoms of different molecules separated by *b*. A two-dimensional network of hydrogen bonds form infinite molecular sheets parallel to the (100) plane. Adjacent sheets are bound together by van der Waals forces.

Introduction

Sulfadiazine is a sulfanilamide derivatives with the systematic name of 2-sulfanilamidopyrimidine. Many sulfanilamide derivatives possess antibacterial activities and sulfadiazine also has a strong antibacterial property. However, the correlation of their pharmacological activities with chemical structures has not satisfactorily been established. Thus far, crystal structures of two sulfanilamide derivatives, sulfathiazole [1,2] and sulfaguanidine monohydrate,[3] have been studied by the single crystal X-ray diffraction method.

The crystal structures of a series of drugs derived from the sulfanilamide have been under study in this laboratory with the object of solving certain relationships between the molecular structures with their pharmacological activities.

Experimental

Colourless needle crystals of the sulfadiazine were grown from its saturated solution in a 1:1 mixture of acetone and ethanol.

Crystallographic data are summarized below;

2-sulfanilamidopyrimidine, $C_{10}H_{10}N_4O_2S$:
F.W.; 250.28
monoclinic
$a=13.71\pm0.04$ Å
$b=5.84\pm0.03$
$c=15.11\pm0.05$
$\beta=115.0\pm0.3°$
$V=1096.4$ Å^3
$D_m=1.52$ g·cm^{-3}
$D_x=1.51$
$Z=4$

Systematic absences; *HOL* when *L* odd and *OKO* when *K* odd

Space group; $P2_1/c$

Unit cell parameters were determined from the *HOL* and *HKO* Weissenberg photographs calibrated with NaCl ($a=5.6396$ Å).

The crystal density was measured by the floatation method in a mixture of benzene and carbon tetrachloride.

The crystal chosen for data collection was approximately cylindrical, 0.3 mm in diameter and 1.0 mm in length, and was mounted with the long dimension coincident with the axis of rotation. Multiple-film equi-inclination Weissenberg data were collected for layer lines *HOL* through *H5L* and *HKO* through *HK*1 with Ni-filtered Cu $K\alpha$ radiation ($\lambda=1.5418$ Å).

Intensities were estimated visually using calibrated intensity strip and were corrected for Lorentz and polarization effects.

The data were correlated and reduced to structure factors without absorption correction, and converted to $|E|$ data with the scale and temperature factors given by Wilson's method[4]. The number of observed independent reflections is 1517.

Determination of the Structure

A three-dimensional sharpened Patterson synthesis was calculated for sections in the *uw* plane computed at fractional intervals of 0.05

in v.

The structure was solved by the heavy atom technique. The positions of S, N(1), O(1), O (2), and C(5) atoms were determined from the Patterson map, and a Fourier synthesis was calculated with 534 reflections phased with the S, N(1), O(1), O(2), C(5) contributions. The seventeen distinctive peaks on the Fourier map were consistent with a predicted model of the sulfadiazine molecule.

Block diagonal least-squares refinement[5] was performed using observed reflections out to sin $\theta/\lambda=0.64$ (536 reflections). This refinement yielded an R index of 0.23. Several cycles of block diagonal least-squares refinement caused the R index for the all observed reflections to converge to 0.15.

The function minimized was $\omega(|F_0|-|F_C|)^2$ and the weighting scheme proposed by Cruickshank[6] was used throughout the refinement. The form of the function, ω, was $(A+B|F_0|+C|F_0|^2)^{-1}$, where $A=3.40$, $B=1.00$, $C=0.016$.

The atomic parameters with their estimated standard deviations are given in *Table* 1, and observed and calculated structure factors are in *Table* 2.

All calculations were performed using IBM 1130 computer, with programs written by Shiono[7]. The atomic scattering factors used were those given by International Tables for X-ray crystallography[8].

Result and Discussion

The bond distances and bond angles with their standard deviations are listed in *Table* 3. The numbering scheme and the bond distances and angles are in *Fig.* 1.

In the benzene ring C–C bond distances vary from the standard value, 1,395 Å. All bond distance deviations are just within the allowed significance range of approximately 2.3σ. The

Table 1. Fractional atomic coordinates and isotropic thermal parameters in sulfadiazine. The estimated standard deviations are given in parentheses and refer to the last decimal positions.

	x	y	z	β
S	0.2350(3)	0.1327(7)	0.4419(3)	2.84(6)
O(1)	0.204(1)	0.362(3)	0.411(1)	3.1(3)
O(2)	0.209(1)	−0.037(3)	0.369(1)	3.8(3)
N(1)	0.368(1)	0.111(3)	0.498(1)	2.9(3)
N(2)	0.395(1)	0.417(3)	0.603(1)	3.2(3)
N(3)	0.539(1)	0.246(3)	0.579(1)	2.9(3)
N(4)	0.066(1)	−0.120(3)	0.733(1)	3.5(3)
C(1)	0.437(1)	0.267(3)	0.564(1)	3.0(3)
C(2)	0.610(2)	0.391(4)	0.641(2)	3.2(4)
C(3)	0.469(2)	0.567(4)	0.665(2)	3.5(4)
C(4)	0.576(2)	0.559(4)	0.686(2)	3.3(4)
C(5)	0.187(1)	0.057(3)	0.527(1)	3.0(3)
C(6)	0.205(2)	−0.153(4)	0.569(1)	3.3(3)
C(7)	0.164(2)	−0.217(4)	0.636(2)	3.4(4)
C(8)	0.105(2)	−0.054(3)	0.663(1)	3.0(3)
C(9)	0.089(2)	0.154(4)	0.622(2)	3.2(4)
C(10)	0.125(2)	0.217(4)	0.552(1)	3.4(3)

Table 2. Observed and calculated structure factors for sulfadiazine. The columns are; index, $|F_{obs}|$, $|F_{clc}|$

$h=0$ $k=0$			2	21.1	14.0	9	15.0	15.0	2	82.7	85.0	$h=2$ $k=5$			8	14.2	9.5	13	23.7	24.4
2	84.0	101.0	3	2.2	0.4	14	4.5	4.2	3	15.9	18.0	0	10.6	12.6	9	5.0	3.0	4	10.7	10.8
4	63.6	73.1	4	7.5	7.5	15	6.7	9.4	4	60.8	60.0	2	11.5	13.8	10	7.5	6.4	5	60.4	60.2
6	31.9	33.3	5	1.7	1.6	$h=1$ $k=3$			5	15.3	14.3	3	4.7	1.0	11	9.3	9.0	6	7.3	9.3
8	21.1	19.3	6	8.9	12.1	0	28.7	28.1	6	5.3	2.1	4	5.7	6.2	12	3.1	2.1	7	13.6	14.2
10	27.3	25.2	7	16.1	13.8	1	8.0	12.3	7	3.7	7.0	6	10.5	7.9	13	8.2	9.4	9	11.2	13.8
14	11.7	13.1	9	3.5	2.7	2	34.8	38.3	8	15.1	19.9	7	8.6	8.8	$h=3$ $k=4$			11	16.0	17.3
16	11.5	13.3	10	4.1	2.8	5	16.8	11.7	9	16.3	20.4	8	8.2	6.9	0	11.4	12.9	13	7.2	9.8
$h=0$ $k=1$			13	4.2	3.7	7	21.3	18.2	10	20.3	23.1	9	9.3	9.2	1	15.6	17.7	14	5.1	5.2
1	43.6	69.0	$h=0$ $k=5$			11	17.3	17.2	11	7.8	8.4	12	2.7	4.5	2	16.8	15.2	$h=4$ $k=3$		
2	6.0	4.9	1	1.7	0.3	$h=1$ $k=4$			12	16.1	19.4	$h=2$ $k=6$			4	22.0	17.8	0	26.9	27.6
3	56.1	50.7	2	24.6	19.0	0	7.9	9.5	13	4.4	6.4	0	11.5	14.1	6	6.2	3.0	1	11.0	8.7
4	15.3	15.3	3	12.3	19.1	1	10.3	11.5	14	9.2	10.4	1	3.8	4.6	8	18.1	18.0	2	28.0	24.5
5	15.6	15.6	4	39.5	43.1	2	11.2	16.9	15	7.2	9.3	$h=3$ $k=0$			9	5.0	7.2	3	18.6	15.3
6	26.3	22.0	5	16.3	11.7	3	15.4	16.9	$h=2$ $k=2$			0	125.5	123.0	11	4.0	5.7	4	27.1	21.1
7	4.0	5.0	6	23.5	18.5	4	32.5	25.7	0	11.4	13.2	2	117.6	121.1	12	2.9	3.0	5	14.1	13.6
9	5.6	6.7	7	11.2	8.5	5	8.9	8.9	1	5.0	7.1	6	7.9	11.5	13	3.1	3.5	6	7.3	10.1
10	8.8	10.5	8	10.8	8.9	6	5.4	4.7	3	36.1	33.8	8	21.7	25.7	$h=3$ $k=5$			7	20.3	18.6
11	20.9	25.9	10	6.2	5.2	7	7.9	9.4	4	20.0	17.0	10	16.1	16.3	0	14.2	16.9	8	7.0	7.3
12	12.0	10.3	12	10.3	9.6	9	5.3	5.4	6	7.0	4.4	12	15.8	17.4	2	2.3	3.2	9	17.6	18.9
15	5.7	9.5	$h=0$ $k=6$			10	8.3	9.3	7	10.2	11.2	$h=3$ $k=1$			4	17.7	16.2	11	6.9	6.5
17	6.2	9.3	0	9.8	10.6	11	5.7	7.3	8	9.8	10.1	0	15.0	17.5	5	6.7	4.6	13	3.0	3.7
$h=0$ $k=2$			$h=1$ $k=0$			12	6.3	7.4	9	8.3	10.2	1	72.2	74.3	6	20.3	17.7	$h=4$ $k=4$		
2	35.5	38.6	4	37.8	36.2	14	3.5	4.8	10	6.3	5.1	2	31.7	30.4	8	9.8	7.2	0	9.1	8.9
3	19.4	16.5	6	9.9	9.0	$h=1$ $k=5$			11	14.3	16.2	3	9.1	4.7	10	3.2	2.7	1	2.0	3.3
5	38.5	39.4	8	7.9	8.3	0	15.9	19.6	13	21.2	29.3	4	13.8	11.4	11	4.2	6.6	3	12.2	10.6
6	45.8	44.8	10	26.5	29.3	2	13.3	10.4	14	4.8	6.5	5	16.3	17.8	$h=3$ $k=7$			4	4.2	2.4
7	7.8	5.5	12	22.2	23.8	5	9.3	7.1	15	8.5	10.5	7	14.4	15.8	0	5.0	6.4	6	17.2	16.8
8	20.2	19.7	14	14.2	13.7	6	13.2	12.0	$h=2$ $k=3$			8	14.9	13.2	$h=4$ $k=0$			8	18.6	19.6
9	5.2	3.8	$h=1$ $k=1$			7	4.5	3.1	0	20.1	21.3	10	7.0	9.3	0	15.7	12.7	9	3.2	5.4
10	4.8	7.7	0	49.8	56.1	8	8.2	6.2	1	25.1	28.3	11	18.6	21.3	2	18.1	21.6	10	10.9	14.6
11	20.6	23.1	1	47.2	44.7	10	7.8	6.6	2	16.0	11.1	12	6.4	6.1	6	30.3	26.0	$h=4$ $k=5$		
13	16.8	18.3	2	29.8	26.4	$h=1$ $k=6$			3	41.1	33.9	13	13.3	18.7	8	15.3	17.4	0	2.5	3.1
14	9.1	10.3	3	49.7	47.4	0	11.6	14.7	4	16.2	10.5	14	6.0	3.7	10	11.5	11.5	1	6.0	5.8
15	5.2	4.1	4	6.4	7.9	1	9.1	16.2	6	7.3	4.7	15	3.2	4.5	$h=4$ $k=1$			2	15.1	16.5
16	4.9	5.5	6	20.3	22.6	$h=1$ $k=7$			7	29.5	26.7	$h=3$ $k=2$			1	7.0	4.9	4	7.0	6.5
$h=0$ $k=3$			8	7.9	6.3	0	4.7	6.4	8	5.7	4.6	0	20.8	16.7	2	33.4	36.0	5	9.9	9.5
1	19.1	27.3	9	6.2	6.7	1	2.1	3.0	9	25.5	21.9	1	36.6	27.8	4	58.8	55.2	9	7.9	7.6
2	39.6	23.6	10	5.4	7.7	$h=2$ $k=0$			10	15.4	12.6	2	10.1	7.5	5	11.9	12.9	10	5.0	5.3
3	18.5	16.2	11	9.0	10.3	0	39.8	41.1	11	5.1	5.0	3	15.8	15.1	7	5.1	7.2	$h=4$ $k=6$		
4	22.4	21.2	12	7.8	8.3	2	130.6	120.5	12	12.0	9.5	4	4.1	4.8	8	7.1	8.6	0	5.7	8.9
6	50.3	45.4	13	10.0	14.3	4	33.3	35.0	15	4.6	5.1	7	33.0	36.8	9	11.2	15.2	1	4.8	7.7
7	28.0	19.7	15	9.3	12.5	6	5.2	7.4	$h=2$ $k=4$			9	13.3	14.1	10	4.7	5.0	$h=4$ $k=7$		
9	13.5	13.6	$h=1$ $k=2$			8	10.1	11.6	0	30.0	29.5	13	6.2	5.9	11	5.1	5.0	1	2.9	6.0
10	38.8	32.3	0	4.5	3.7	10	5.7	4.4	1	4.6	7.6	$h=3$ $k=3$			12	6.1	6.9	$h=5$ $k=0$		
11	9.5	10.6	2	43.3	36.9	12	15.3	17.9	2	29.4	28.4	0	22.8	21.1	14	7.8	11.5	0	77.1	83.3
12	19.7	14.1	3	84.5	85.3	14	10.6	6.3	3	12.8	9.6	1	7.7	5.2	15	6.0	7.9	2	87.0	79.6
15	8.4	8.8	5	17.9	16.7	16	6.8	8.7	4	10.6	10.0	2	17.8	15.2	$h=4$ $k=2$			4	22.7	18.8
$h=0$ $k=4$			6	28.5	27.1	$h=2$ $k=1$			5	8.2	5.9	3	9.4	5.7	0	5.5	4.0	10	7.2	4.4
0	36.1	37.2	7	13.2	12.8	0	8.6	8.3	6	25.4	25.4	5	16.5	14.8	1	32.5	27.8	12	8.4	7.0
1	6.0	6.1	8	4.3	3.1	1	90.2	93.4	8	26.8	25.9	6	12.5	11.5	2	17.4	14.3	$h=5$ $k=1$		

0	6.5	7.7	0	57.9	58.4	0	1.8	4.0	2	10.6	7.7	0	6.1	5.7	3	18.9	16.7	9	10.0	10.8
1	14.4	11.6	2	40.3	38.7	h=7 k=0			4	11.4	8.9	1	17.9	15.4	4	12.2	9.7	10	8.8	8.7
2	14.5	12.9	4	10.0	10.1	0	52.4	53.3	6	7.4	6.9	2	19.1	15.4	5	6.8	5.1	12	11.4	13.8
3	61.8	86.2	6	14.8	11.9	2	24.8	18.9	7	13.7	15.7	3	24.5	20.6	h=11 k=4			13	11.6	13.4
4	43.9	41.9	8	30.1	30.3	4	8.9	2.9	9	11.8	11.5	4	10.3	8.7	0	12.2	9.0	15	3.0	4.1
5	12.8	14.3	12	7.4	6.5	6	6.5	7.7	10	7.7	8.2	5	5.2	4.9	h=12 k=4			16	9.0	10.6
6	12.6	11.5	h=6 k=1			8	17.4	21.6	11	5.2	7.0	6	10.5	8.3	0	12.2	9.0	h=−1 k=2		
7	13.9	15.1	0	21.7	18.4	12	9.3	8.0	h=8 k=2			7	11.0	10.4	h=12 k=0			1	24.9	37.5
8	6.1	4.7	2	6.3	7.5	h=7 k=1			1	24.2	23.1	8	4.8	3.2	0	8.3	9.6	2	11.1	7.8
11	14.5	14.3	3	9.2	9.1	0	42.4	41.7	2	10.0	8.1	9	6.2	7.6	2	19.4	17.4	3	2.7	4.8
13	6.5	6.2	4	5.6	4.0	1	24.8	22.9	3	28.9	26.4	h=9 k=4			4	12.1	11.7	4	12.5	9.7
14	4.5	7.0	6	19.8	19.6	3	15.0	15.9	4	8.9	9.4	2	11.1	11.6	6	7.7	5.6	5	36.4	32.4
h=5 k=2			7	10.1	9.3	4	29.8	31.8	9	4.5	4.1	3	7.2	8.4	h=12 k=1			6	4.0	2.7
0	21.7	19.9	9	9.3	9.9	5	31.1	33.3	h=8 k=3			4	4.6	4.0	1	5.1	6.5	7	21.0	20.9
1	3.5	4.8	11	6.0	7.4	6	30.2	30.5	1	22.0	19.8	5	2.9	3.4	2	8.3	9.5	8	13.3	10.9
3	25.6	24.0	13	5.4	7.6	12	5.9	6.1	2	16.3	12.1	h=9 k=5			3	9.8	12.6	9	26.6	25.1
4	7.0	7.7	h=6 k=2			h=7 k=2			3	12.4	12.4	0	12.9	11.4	h=12 k=2			10	10.1	9.4
5	18.7	19.1	0	6.2	5.8	0	16.8	16.9	4	15.6	12.5	1	8.5	9.6	1	8.9	11.7	11	27.0	30.0
7	10.7	10.8	1	21.9	17.3	1	19.7	18.0	5	8.6	8.7	h=10 k=0			h=12 k=3			12	14.2	14.5
8	8.5	6.2	2	24.4	22.9	2	7.0	7.8	6	6.8	4.8	0	5.7	8.3	1	3.5	5.7	14	12.9	16.0
9	18.8	19.2	3	36.1	33.9	3	15.6	12.8	7	12.1	11.7	2	11.8	11.9	h=12 k=4			15	9.0	9.7
10	5.0	5.6	5	40.6	39.1	5	28.2	27.5	9	6.7	5.7	4	11.4	15.5	1	3.7	4.2	17	4.2	7.5
13	6.2	6.7	6	15.2	16.9	6	6.0	6.8	h=8 k=4			6	10.1	7.8	h=12 k=5			h=−1 k=3		
h=5 k=3			7	16.3	14.6	7	22.2	19.4	0	12.5	14.2	8	10.4	10.4	0	5.7	5.8	1	15.0	20.9
1	3.0	2.3	9	6.5	6.5	9	5.1	3.8	1	4.0	6.4	k=10 k=1			h=13 k=2			3	5.9	7.3
2	31.3	26.0	11	10.3	12.8	10	4.2	5.8	2	12.9	14.7	0	27.5	24.8	0	4.2	5.0	4	10.6	6.2
3	33.8	27.7	h=6 k=3			h=7 k=3			3	7.1	7.6	5	12.4	13.4	h=13 k=3			5	40.6	33.4
4	14.2	12.5	0	20.0	20.3	0	3.2	1.8	4	7.0	8.3	2	9.1	8.7	0	6.3	5.6	6	15.4	15.1
5	24.7	21.3	1	29.1	26.3	1	19.0	15.6	6	7.2	6.9	4	6.6	5.4	1	8.5	11.9	7	37.2	32.7
6	26.0	21.7	2	34.1	30.1	2	5.2	2.9	h=8 k=5			6	9.5	10.8	h=13 k=4			8	14.4	10.6
8	13.0	8.9	2	9.8	8.4	3	24.6	19.0	0	22.1	22.0	7	5.8	5.4	0	9.5	9.5	9	4.7	4.0
9	14.4	13.3	4	15.8	12.1	5	8.0	8.4	h=8 k=6			8	5.5	5.9	h=14 k=0			11	8.1	5.4
10	5.4	3.7	5	12.5	10.5	6	8.6	5.6	1	2.9	4.8	h=10 k=2			0	5.2	3.8	15	10.3	8.8
11	6.7	4.8	6	22.7	18.0	9	8.2	7.2	h=9 k=0			2	11.0	11.3	h=14 k=1			h=−1 k=4		
13	4.1	5.0	7	23.8	20.2	11	7.5	9.5	0	25.5	25.6	3	13.0	14.1	0	7.8	6.5	1	10.9	9.4
h=5 k=4			9	7.2	5.9	h=7 k=4			2	28.9	25.7	5	7.1	4.6	h=14 k=2			2	23.4	20.7
0	19.7	20.7	10	6.3	3.3	0	31.0	33.2	4	15.7	17.1	6	5.7	5.4	1	12.3	15.8	3	4.3	7.2
1	3.9	5.8	11	4.1	4.1	1	21.3	19.6	8	22.5	21.8	7	11.2	11.8	h=14 k=3			4	26.1	23.6
2	19.2	18.1	h=6 k=4			2	23.9	23.4	10	4.0	7.2	h=10 k=3			0	7.5	7.2	6	39.4	38.9
3	7.8	6.1	0	25.5	23.0	3	8.2	9.1	h=9 k=1			1	4.4	2.6	h=15 k=0			7	18.7	13.1
4	12.6	13.5	1	10.7	9.9	4	13.3	13.9	1	30.4	31.9	3	6.4	4.9	0	4.8	3.2	8	18.9	17.5
6	3.7	3.6	3	9.7	11.6	5	7.3	5.9	4	5.7	7.3	h=10 k=4			h=−1 k=0			10	9.1	8.1
7	4.9	4.7	4	10.7	11.4	8	2.9	3.0	7	7.5	7.8	1	11.0	13.5	2	41.7	43.5	11	5.2	3.9
8	4.4	6.3	6	7.8	8.1	9	4.9	6.1	8	7.4	5.3	k=10 k=5			6	13.1	14.9	12	13.3	13.3
h=5 k=5			9	4.1	4.5	h=7 k=5			9	6.7	8.1	0	3.5	1.3	8	27.1	26.4	13	5.0	5.3
0	12.6	13.2	10	2.2	3.1	0	7.3	6.4	h=9 k=2			h=11 k=1			14	9.1	8.4	14	7.5	7.3
2	8.1	7.0	h=6 k=5			1	5.5	7.0	0	7.7	6.4	3	8.5	10.5	h=−1 k=1			15	2.5	2.8
3	12.8	14.1	1	6.7	8.3	3	8.1	10.9	1	37.5	34.6	4	12.6	12.5	1	44.2	73.1	h=−1 k=5		
4	15.8	14.2	2	7.9	8.8	5	13.0	14.4	2	23.7	22.5	6	8.3	6.2	2	98.5	114.4	1	2.9	2.8
5	6.8	6.6	4	11.1	11.5	h=7 k=6			4	6.0	3.7	h=11 k=2			3	95.1	95.9	2	4.4	4.1
6	9.3	5.3	5	4.5	4.8	0	7.8	7.9	5	14.7	13.8	3	8.5	8.4	4	51.8	51.8	3	10.9	20.3
8	8.8	8.3	7	4.5	5.0	h=8 k=0			6	11.6	12.2	4	7.3	7.4	5	4.6	6.0	4	18.8	19.2
h=5 k=6			h=6 k=6			4	29.8	27.5	7	22.0	21.1	5	19.8	18.4	6	20.4	23.8	5	10.8	9.5
1	3.1	3.9	1	6.2	10.7	h=8 k=1			8	6.5	7.9	h=11 k=3			7	7.9	8.7	10	7.4	4.7
h=6 k=0			h=6 k=7			0	9.4	9.4	h=9 k=3			1	15.6	11.7	8	39.0	44.3	13	6.3	4.7

$h=-1$ $k=6$			15	11.3	11.4	6	53.4	53.7	12	6.3	6.5	10	15.0	14.2	18	4.5	4.8	12	27.2	25.8
1	5.0	8.9	$h=-2$ $k=4$			7	33.0	31.6	18	5.4	5.2	11	10.2	7.9	$h=-5$ $k=3$			14	11.8	12.8
$h=-1$ $k=7$			2	57.1	37.5	8	11.6	14.0	$h=-4$ $k=1$			12	13.5	12.6	1	13.6	9.0	16	11.3	10.6
1	4.8	6.7	3	12.6	16.9	9	27.9	27.4	1	49.1	43.2	15	5.5	4.4	2	16.5	11.2	18	10.7	10.3
$h=-2$ $k=0$			4	13.4	11.8	11	18.6	20.0	2	39.3	40.3	$h=-4$ $k=5$			3	12.1	8.7	$h=-6$ $k=1$		
2	35.5	38.9	4	5.1	2.2	13	12.0	14.4	3	8.5	4.5	1	16.1	13.0	4	2.3	2.8	1	5.8	8.6
4	25.2	30.0	6	25.6	20.9	14	15.4	17.1	4	15.7	13.2	2	22.2	20.5	5	8.8	1.8	2	28.1	34.9
6	37.9	41.1	7	10.0	10.8	15	8.1	7.7	5	54.7	53.3	3	3.9	5.7	6	2.4	0.5	3	11.0	12.7
8	46.4	41.0	8	37.7	35.4	16	4.3	4.8	6	45.7	41.2	4	20.6	17.3	7	28.3	25.4	4	14.6	13.1
10	30.4	29.8	9	13.4	15.4	17	6.6	10.7	7	39.7	43.9	5	12.2	8.0	8	42.7	38.2	5	21.2	19.8
12	8.6	6.8	10	15.1	16.3	$h=-3$ $k=3$			8	23.4	21.8	6	15.5	13.7	9	12.8	12.4	6	47.8	44.5
16	7.1	5.1	11	6.0	8.1	1	5.2	6.5	9	6.9	6.2	7	13.1	9.2	10	21.5	18.9	7	13.8	16.5
$h=-2$ $k=1$			12	8.1	9.0	2	29.8	26.4	11	22.6	25.6	9	6.6	6.3	11	19.2	14.2	8	4.4	5.6
1	43.3	41.8	13	9.6	10.6	4	30.4	25.9	12	14.9	16.7	1	6.8	3.3	12	6.1	3.7	9	12.6	11.8
2	54.6	57.7	14	4.7	7.6	5	33.9	24.1	13	13.1	17.6	11	15.6	11.5	13	23.7	17.9	10	25.7	28.7
3	30.5	29.7	$h=-2$ $k=5$			7	16.4	13.9	14	7.4	7.1	12	14.7	12.0	14	9.5	7.4	11	10.8	10.3
4	100.6	109.9	1	7.1	7.8	8	30.7	27.0	16	5.9	5.8	13	8.6	4.4	15	12.6	11.1	12	20.9	22.9
5	20.1	17.4	2	36.5	26.3	9	24.3	25.7	18	4.9	4.7	14	9.0	9.0	16	3.7	3.9	15	6.0	9.0
6	26.9	29.7	3	9.4	10.7	10	56.6	53.1	$h=-4$ $k=2$			$h=-5$ $k=0$			17	4.0	4.3	17	7.2	8.3
7	11.5	12.7	4	24.5	28.9	12	9.2	6.7	1	7.2	6.5	2	12.1	11.3	$h=-5$ $k=4$			19	5.2	7.7
9	21.8	26.3	6	11.1	6.1	13	12.9	12.3	2	7.1	12.5	4	76.5	81.6	1	17.6	15.4	$h=-6$ $k=2$		
10	15.3	17.2	7	5.3	2.8	14	7.3	6.0	4	19.5	20.8	6	41.2	41.9	2	16.3	19.1	1	12.5	15.6
11	11.4	13.0	8	10.0	7.1	15	14.8	13.3	5	13.6	14.9	8	9.8	7.1	3	9.0	6.4	4	36.3	31.1
12	12.0	11.2	10	5.7	3.4	17	5.6	4.9	7	25.1	21.7	10	24.1	24.1	4	23.9	20.7	5	5.7	4.3
13	13.1	17.4	11	5.7	4.6	$h=-3$ $k=4$			8	18.8	15.5	14	22.4	27.2	5	6.7	4.4	6	13.8	12.2
14	7.3	7.5	13	10.5	9.1	1	3.6	5.2	9	4.5	5.6	16	9.0	5.8	6	31.5	25.9	7	6.7	8.3
15	3.8	5.6	$h=2$ $k=6$			2	13.5	16.0	10	7.9	7.9	$h=-5$ $k=1$			7	18.5	17.0	8	8.8	6.1
17	10.2	12.3	1	5.7	7.1	3	13.8	15.8	12	21.2	21.5	2	37.7	33.9	8	21.0	19.1	9	14.7	13.6
18	4.2	4.8	$h=-3$ $k=0$			4	23.6	20.7	13	23.2	25.3	3	3.6	3.1	9	15.0	13.1	11	11.6	11.2
$h=-2$ $k=2$			2	60.8	62.7	5	6.4	5.3	14	10.1	10.4	4	10.0	18.0	10	10.2	10.1	13	7.0	7.1
1	16.5	15.2	4	105.3	116.9	6	26.8	23.2	15	7.4	8.1	5	12.4	11.0	11	5.3	4.3	15	12.1	12.7
2	49.1	45.7	6	23.3	29.5	7	4.9	6.5	16	4.0	3.6	6	13.8	10.8	12	12.6	13.9	17	8.2	10.3
3	21.8	18.8	8	33.8	28.7	9	4.7	5.6	$h=-4$ $k=3$			7	11.8	12.9	13	7.2	8.6	$h=-6$ $k=3$		
4	15.4	14.7	10	20.5	24.4	11	4.6	4.3	1	5.9	3.9	8	25.4	27.9	14	13.9	15.0	1	3.1	3.8
5	38.0	36.2	12	21.4	22.1	12	4.0	4.4	2	31.9	25.4	9	17.8	17.4	16	5.4	4.4	2	14.6	10.5
6	32.3	35.6	14	15.4	15.0	15	6.0	6.1	3	8.0	88.7	10	32.2	33.4	$h=-5$ $k=5$			3	3.4	3.1
7	51.0	52.0	16	18.9	18.1	$h=-3$ $k=5$			4	19.9	14.6	12	17.0	20.9	1	3.4	3.6	4	3.4	3.9
10	7.1	8.3	$h=-3$ $k=1$			1	8.5	10.8	5	22.0	16.3	13	9.6	12.4	2	39.7	34.3	5	7.2	8.0
11	18.8	17.4	1	30.6	26.0	2	13.9	18.1	6	9.3	8.6	15	10.0	13.8	3	14.5	9.3	6	21.8	18.0
12	6.6	7.7	2	16.6	16.6	4	22.9	23.4	7	11.8	9.2	16	9.6	11.1	4	13.7	9.5	8	25.3	20.9
15	8.7	10.0	4	6.4	5.1	5	10.9	11.1	9	25.8	21.3	18	6.0	6.3	5	6.5	5.6	11	8.0	6.2
$h=-2$ $k=3$			5	12.5	12.7	6	8.9	6.2	10	8.1	10.7	$h=-5$ $k=2$			6	11.3	9.8	12	16.5	16.3
1	4.6	8.8	6	45.8	39.4	7	11.9	9.8	12	11.9	10.4	1	11.6	14.9	7	13.0	9.6	13	9.3	9.2
2	12.6	16.2	7	9.2	12.2	8	19.8	15.6	16	5.9	4.8	2	21.1	2.0	8	10.5	7.5	15	5.8	4.7
3	7.3	9.2	8	11.1	14.5	10	12.7	9.1	17	3.4	2.9	3	32.9	29.0	9	7.2	5.2	17	4.2	4.0
4	33.5	32.6	9	23.2	25.4	11	9.0	7.1	$h=-4$ $k=4$			4	6.4	2.4	10	13.5	9.1	$h=-6$ $k=4$		
5	5.4	5.0	10	19.1	20.4	12	11.1	8.2	1	33.5	26.0	5	19.1	19.8	$h=-5$ $k=6$			2	16.4	13.3
6	7.1	3.5	11	4.8	6.1	$h=-3$ $k=7$			2	23.8	22.2	6	7.1	5.1	1	7.9	14.2	4	7.9	7.3
7	8.1	5.4	13	9.1	12.9	1	3.4	5.3	3	20.6	18.6	7	15.7	12.6	$h=-5$ $k=7$			5	19.9	17.0
8	2.8	4.6	14	3.3	3.6	$h=-4$ $k=0$			4	13.6	11.1	8	9.6	12.7	1	2.8	4.7	6	10.4	8.4
9	26.9	23.3	$h=-3$ $k=2$			2	63.5	66.2	5	5.4	3.9	9	24.5	26.0	$h=-6$ $k=0$			7	3.1	3.4
11	14.4	11.8	1	16.5	14.7	4	13.4	10.6	6	11.7	10.1	11	20.3	19.4	2	46.4	49.0	8	5.5	3.9
12	4.7	4.8	2	33.8	29.6	6	74.4	64.7	7	4.0	4.5	12	16.1	18.4	4	7.1	8.5	9	17.2	14.3
13	7.4	5.9	4	18.2	18.2	8	81.6	79.6	8	34.3	30.6	13	20.7	23.3	6	43.9	44.3	10	20.4	20.7
14	15.3	11.6	5	28.7	21.9	10	19.9	20.8	9	3.5	1.5	17	4.7	6.2	10	22.9	21.9	11	3.9	1.7

12	10.4	8.7	5	5.8	5.3	19	5.6	8.6	4	51.4	43.9	8	18.5	16.8	8	9.4	8.4	6	13.2	9.5
13	3.9	1.5	6	5.1	4.3	$h=-8$ $k=2$			6	45.8	40.5	9	10.9	8.3	10	10.1	9.0	7	11.9	12.5
16	6.9	9.0	7	25.3	18.7	2	9.6	9.0	8	46.5	46.3	10	10.5	9.4	11	14.0	11.1	9	4.7	5.1
$h=-6$ $k=5$			8	12.0	10.7	3	28.4	26.4	10	19.9	20.9	11	6.3	3.8	12	7.2	4.4	10	14.7	14.2
2	4.2	4.1	12	9.1	6.5	4	8.5	5.1	12	14.7	16.9	12	5.3	4.9	13	6.6	4.1	13	13.0	10.1
3	4.6	4.3	13	11.7	10.4	6	16.7	16.5	14	12.4	11.8	14	10.3	10.7	15	8.2	6.2	$h=-11$ $k=3$		
4	15.2	12.8	15	10.2	7.7	7	15.9	14.1	16	15.7	13.4	16	5.1	8.4	$h=-10$ $k=4$			2	5.9	4.4
5	2.7	4.2	16	4.1	5.0	8	6.7	5.5	$h=-9$ $k=1$			$h=-9$ $k=5$			1	6.4	3.4	3	12.6	9.5
6	17.5	13.1	17	11.8	10.9	9	4.3	3.9	2	12.2	12.3	2	23.8	15.5	2	13.1	9.7	5	11.3	7.3
7	10.5	6.3	$h=-7$ $k=4$			10	18.3	17.6	3	27.6	22.2	3	11.8	7.6	3	8.4	7.6	6	39.5	27.1
9	21.1	13.2	1	23.9	16.8	12	12.3	14.0	4	27.4	27.0	4	26.9	23.8	4	34.8	29.4	7	30.6	18.3
10	5.3	3.1	2	6.3	4.7	15	10.3	7.2	5	35.7	34.6	5	16.4	11.9	5	15.5	12.9	9	12.7	8.5
11	9.0	6.8	4	13.6	9.3	17	9.9	11.0	6	5.3	6.6	7	7.8	4.5	6	25.1	21.0	10	10.6	9.7
12	6.6	5.9	6	40.1	32.1	$h=-8$ $k=3$			7	15.4	15.6	8	23.5	14.4	7	6.7	6.4	12	13.4	9.5
13	4.4	3.1	8	18.7	17.2	1	18.2	13.8	9	8.1	8.0	9	8.4	5.6	8	6.7	6.1	13	10.0	6.7
14	7.8	6.7	6	5.1	3.3	2	23.4	19.0	10	21.3	25.1	10	15.6	11.0	9	7.3	5.5	14	9.0	6.9
$h=-7$ $k=0$			10	3.1	2.7	3	24.0	15.9	16	4.1	5.5	12	9.1	7.7	10	16.2	15.3	15	3.9	3.0
2	14.2	19.4	12	20.3	19.2	5	7.6	3.2	17	5.2	4.1	$h=-9$ $k=6$			12	15.0	14.4	$h=-11$ $k=4$		
6	52.2	50.1	13	3.1	4.3	6	29.7	24.3	15	9.5	8.0	1	4.6	6.9	14	7.7	6.5	4	15.0	12.1
8	10.6	14.1	14	11.4	13.0	7	4.5	4.4	18	5.8	5.7	$h=-10$ $k=0$			$h=-10$ $k=5$			6	22.1	15.8
10	7.9	7.1	16	6.7	7.7	8	34.5	28.1	$k=-9$ $k=2$			2	27.9	26.1	1	10.4	8.3	7	8.8	5.6
13	22.3	26.0	$h=-7$ $k=5$			9	11.7	5.8	1	21.1	18.9	4	25.7	24.5	2	3.7	1.9	8	24.4	17.4
14	20.5	21.9	1	4.3	5.6	10	8.9	6.5	2	7.3	4.4	8	14.2	15.5	3	5.2	2.8	9	7.9	5.4
$h=-7$ $k=1$			2	23.3	18.5	11	11.9	10.6	3	15.2	10.8	18	11.4	11.5	5	8.6	5.2	10	4.3	4.3
1	42.2	38.2	3	4.7	3.8	13	6.9	8.0	4	12.8	11.5	$h=-10$ $k=1$			6	12.4	9.6	12	7.0	5.1
2	45.1	42.4	4	18.1	13.4	14	20.3	14.6	5	22.9	20.1	1	11.2	9.0	8	4.9	3.1	14	9.4	11.8
3	29.4	25.6	5	13.4	8.6	15	3.3	2.8	6	19.7	16.3	2	4.4	2.1	11	4.8	4.8	$h=-11$ $k=5$		
4	38.2	37.1	6	10.6	6.7	16	8.0	6.2	7	7.4	5.7	3	19.2	18.8	12	3.7	3.3	2	17.0	12.4
5	40.2	36.1	8	9.9	7.0	$h=-8$ $k=4$			8	10.2	9.2	6	15.7	12.5	$h=-11$ $k=0$			3	7.0	4.9
6	15.9	14.8	9	8.9	5.1	1	11.3	9.7	9	21.0	20.8	7	18.2	20.3	4	9.9	4.2	4	6.9	5.8
7	8.8	7.9	10	16.5	11.3	2	16.2	13.6	10	10.9	10.6	8	44.4	37.0	6	44.1	40.6	9	9.9	8.6
8	26.1	26.4	12	9.9	7.6	3	4.7	3.4	11	10.7	9.8	9	20.2	19.9	8	34.4	33.8	10	7.1	4.7
9	6.9	10.1	$h=-7$ $k=6$			4	9.6	8.9	12	9.0	6.8	10	41.3	40.9	12	18.0	19.0	11	4.2	3.0
10	28.2	30.2	1	7.5	15.3	5	2.4	3.8	17	9.6	8.4	13	9.7	12.7	16	24.4	20.9	12	11.3	13.2
11	15.3	17.4	$h=-8$ $k=0$			6	20.3	16.8	18	3.4	2.8	14	15.9	16.8	18	10.9	9.2	$h=-12$ $k=0$		
12	19.5	20.9	2	53.8	42.4	7	19.0	16.8	$h=-9$ $k=3$			16	11.4	11.9	$h=-11$ $k=1$			2	7.8	2.7
15	11.2	14.0	4	56.3	55.8	8	7.5	7.1	2	45.4	35.7	17	5.9	4.4	2	15.2	16.0	4	33.0	25.0
16	5.7	7.4	6	14.7	16.3	9	3.3	4.0	3	11.1	7.7	18	4.1	2.4	3	9.2	10.4	6	18.0	19.0
17	9.2	11.1	8	26.9	27.1	10	16.8	14.2	4	29.1	21.7	$h=-10$ $k=2$			4	15.0	13.3	8	16.8	17.1
18	6.8	8.5	10	11.5	11.7	11	12.4	10.3	5	18.9	11.7	4	21.8	17.6	5	20.6	20.3	10	15.1	13.6
$h=-7$ $k=2$			12	12.0	10.8	14	3.7	6.2	7	4.5	2.8	5	27.8	26.2	6	9.7	11.2	12	31.9	33.5
1	35.6	34.3	16	11.1	11.0	15	3.7	4.0	8	6.3	6.2	6	14.2	12.2	7	27.7	24.9	14	22.9	21.3
2	9.9	9.5	18	12.7	14.2	$h=-8$ $k=5$			9	14.3	12.1	7	27.4	24.9	8	25.5	21.9	16	5.6	7.8
3	6.8	4.5	$h=-8$ $k=1$			1	5.2	2.8	10	20.3	18.1	9	16.1	13.7	9	11.9	11.9	18	6.4	5.3
4	18.2	17.0	1	16.8	16.2	2	9.9	6.2	12	7.3	5.1	11	15.6	16.5	10	17.6	18.3	$h=-12$ $k=1$		
5	19.3	16.9	2	5.5	9.9	3	4.9	4.1	13	5.5	5.3	13	8.6	6.6	12	6.6	7.5	1	8.8	10.1
6	13.5	13.6	3	10.1	12.1	4	12.3	10.9	14	6.9	9.1	14	4.0	3.4	13	7.6	7.3	3	17.2	16.1
9	15.3	12.8	4	23.6	20.3	5	9.4	5.5	15	8.3	8.1	15	9.0	6.0	16	8.5	8.7	4	7.0	4.9
10	10.2	8.0	6	9.7	10.5	6	9.2	6.3	16	9.5	8.2	18	3.2	3.9	17	6.2	5.7	6	14.9	11.4
11	38.7	34.8	7	6.7	6.7	7	12.2	9.5	$h=-9$ $k=4$			$h=-10$ $k=3$			18	6.8	8.6	7	5.7	6.1
12	8.1	8.4	9	6.6	7.2	8	11.3	7.8	1	4.7	2.6	1	26.8	21.2	$h=-11$ $k=2$			8	20.2	17.3
15	12.0	11.7	13	9.7	11.6	12	4.1	3.2	3	19.2	18.2	2	35.4	24.7	1	22.2	19.0	9	10.0	9.6
17	6.8	8.7	14	11.7	12.1	14	6.3	9.1	4	7.0	5.4	4	17.0	12.3	2	12.7	10.9	11	6.2	7.3
$h=-7$ $k=3$			16	6.3	6.5	$h=-9$ $k=0$			6	14.3	11.0	6	6.3	4.6	3	26.1	23.9	12	7.6	6.1
4	10.3	9.4	17	9.7	12.7	2	13.0	15.0	7	21.2	14.4	7	3.8	3.3	4	8.9	6.5	15	8.8	10.5

17	4.3	5.5	1	3.1	3.3	5	16.9	12.9	5	5.1	3.3	7	9.6	8.2	14	9.3	7.7	4	22.7	21.7
18	4.7	5.6	2	7.5	5.2	6	7.8	7.2	6	4.6	3.0	13	6.0	5.3	$h=-15$ $k=1$			6	12.5	12.0
$h=-12$ $k=2$			3	10.5	8.7	7	9.9	12.8	8	7.8	7.7	15	11.8	9.9	1	11.5	9.9	8	6.7	6.6
1	8.6	7.4	4	7.6	5.3	8	9.6	10.0	10	12.2	12.0	$h=-14$ $k=3$			2	11.6	9.8	10	8.3	6.1
3	11.8	8.5	5	8.8	6.5	9	7.3	7.5	$h=-13$ $k=5$			1	5.7	3.8	4	12.7	9.6	12	6.1	3.7
5	15.6	12.1	7	10.7	9.0	12	19.0	16.7	5	2.5	0.8	2	7.7	5.6	10	5.5	4.8	14	11.2	10.1
6	12.6	11.5	9	6.4	6.1	14	14.0	13.2	$h=-14$ $k=0$			3	14.3	9.2	12	8.7	7.0	$h=-16$ $k=1$		
7	13.5	10.5	10	11.1	9.2	15	8.9	9.4	2	8.5	5.9	5	12.3	7.9	14	7.7	7.4	1	4.1	2.5
8	5.2	8.2	12	12.0	12.8	16	6.0	5.2	4	13.1	8.2	8	6.3	5.0	15	4.4	4.3	2	8.3	6.7
9	28.3	25.5	14	8.4	11.0	17	10.5	11.7	6	26.7	25.6	9	12.1	6.7	$h=-15$ $k=2$			3	10.6	9.9
10	12.4	9.6	$k=-12$ $k=5$			$h=-13$ $k=2$			10	14.0	13.6	11	15.0	11.4	1	7.8	6.1	4	5.5	5.7
12	10.3	8.1	1	4.4	3.6	1	14.8	15.1	12	11.6	10.5	13	8.2	7.2	2	5.5	4.2	5	14.7	14.3
13	6.7	5.3	2	17.2	14.6	2	7.2	6.9	14	8.8	7.5	14	5.0	4.4	3	14.3	12.6	8	5.2	3.9
15	11.1	9.3	3	8.8	6.5	3	12.3	9.5	16	15.4	14.1	$h=-14$ $k=4$			5	11.3	8.7	10	10.8	9.9
17	8.3	8.3	4	7.5	5.6	4	8.8	5.7	$h=-14$ $k=1$			2	5.9	4.9	7	10.4	8.4	11	5.5	5.0
$h=-12$ $k=3$			6	11.3	7.4	5	9.3	7.0	2	7.3	9.0	3	3.3	3.0	9	7.6	5.4	13	6.8	5.5
1	3.9	4.7	8	18.1	15.5	7	5.5	5.9	3	11.7	10.6	4	3.3	2.3	10	4.7	4.8	$h=-16$ $k=2$		
2	16.9	10.6	9	9.9	8.7	9	5.8	5.6	4	5.4	6.5	5	4.9	3.8	11	13.5	10.8	4	3.1	1.8
6	17.6	12.8	10	8.1	6.7	10	5.7	4.5	5	23.2	21.4	6	9.7	9.0	12	7.6	8.0	5	5.0	4.7
7	4.4	2.6	11	4.1	4.9	11	17.2	12.4	6	5.9	5.0	7	3.2	2.9	13	6.7	4.7	7	11.0	9.6
8	21.2	14.3	$h=-13$ $k=0$			13	9.4	7.3	8	14.7	14.0	8	2.0	2.6	$h=-15$ $k=3$			9	6.7	5.2
9	4.3	3.2	2	12.3	13.5	$h=-13$ $k=3$			9	14.0	14.1	9	4.7	3.9	2	11.3	6.5	$h=-17$ $k=0$		
10	11.9	8.5	4	17.7	16.4	1	8.6	6.6	10	4.3	5.5	10	8.8	6.9	4	8.1	5.3	4	10.6	12.8
11	16.6	9.21	6	32.5	31.6	4	9.7	6.5	13	7.2	6.8	$h=-15$ $k=0$			5	4.2	3.8	8	11.4	10.5
13	16.5	11.7	12	15.3	13.2	5	14.9	11.5	14	13.7	10.5	2	10.3	7.2	8	5.1	5.1	10	6.9	6.9
14	7.8	7.4	14	19.4	16.9	10	12.2	7.9	15	6.2	4.1	4	6.1	4.5	9	3.2	2.5	$h=-17$ $k=1$		
15	3.9	3.7	16	10.7	9.8	12	18.3	13.6	16	12.4	13.1	6	10.4	11.2	11	6.1	2.8	6	4.5	3.8
16	7.7	6.4	$h=-13$ $k=1$			$h=-13$ $k=4$			$h=-14$ $k=2$			8	5.8	6.6	$h=-16$ $k=0$			7	8.2	7.3
$h=-12$ $k=4$			1	9.0	7.9	2	4.6	3.4	1	11.0	10.4	10	8.3	7.6	2	8.1	5.9	9	5.8	5.7

Table 3. Interatomic distances (Å) and bond angles(°) in the sulfadiazine*

Bond distances

C(1)—N(1)	1.38(3)	C(3)—N(2)	1.37(3)	C(8)—N(4)	1.43(3)
C(1)—N(2)	1.31(3)	C(5)—C(6)	1.35(3)	C(9)—C(10)	1.39(3)
C(1)—N(3)	1.33(2)	C(5)—C(10)	1.42(3)	S —C(5)	1.74(2)
C(2)—C(4)	1.38(3)	C(6)—C(7)	1.41(3)	S —N(1)	1.66(2)
C(2)—N(3)	1.33(3)	C(7)—C(8)	1.41(3)	S —O(1)	1.42(2)
C(3)—C(4)	1.36(3)	C(8)—C(9)	1.33(3)	S —O(2)	1.41(2)

Bond angles

N(1)—C(1)—N(2)	118(2)	C(5)—C(6)—C(7)	121(2)	C(1)—N(3)—C(2)	118(2)
N(1)—C(1)—N(3)	114(2)	C(6)—C(7)—C(8)	119(2)	O(1)— S —C(5)	109(1)
N(2)—C(1)—N(3)	128(2)	C(7)—C(8)—C(9)	119(2)	C(1)— S —N(1)	111(1)
N(3)—C(2)—C(4)	120(2)	C(7)—C(8)—C(4)	118(2)	O(1)— S —O(2)	118(1)
N(2)—C(3)—C(4)	123(2)	C(9)—C(8)—N(4)	123(2)	O(2)— S —C(5)	110(1)
C(2)—C(4)—C(3)	118(2)	C(8)—C(9)—C(10)	123(2)	O(2)— S —N(1)	102(1)
C(6)—C(5)— S	121(1)	C(5)—C(10)—C(9)	118(2)	C(5)— S —N(1)	107(1)
C(6)—C(5)—C(10)	119(2)	C(1)—N(1)— S	125(1)		
C(10)—C(5)— S	119(1)	C(1)—N(2)—C(3)	113(2)		

*The estimated standard deviations given in parentheses are for last significant figures

standard deviations, σ, in these distances are all 0.03 Å.

The bond angles in the benzene ring differ slightly from the theoretical value of 120°.

The C(8)—N(4) bond distance is 1.43(3) Å long, in good agreement with the corresponding bond in sulfathiazole III[2], and appreciably shorter than the 1.470(5) Å proposed by Camerman[9] for the length of a $C(sp^2)$—$N(sp^2)$ single bond.

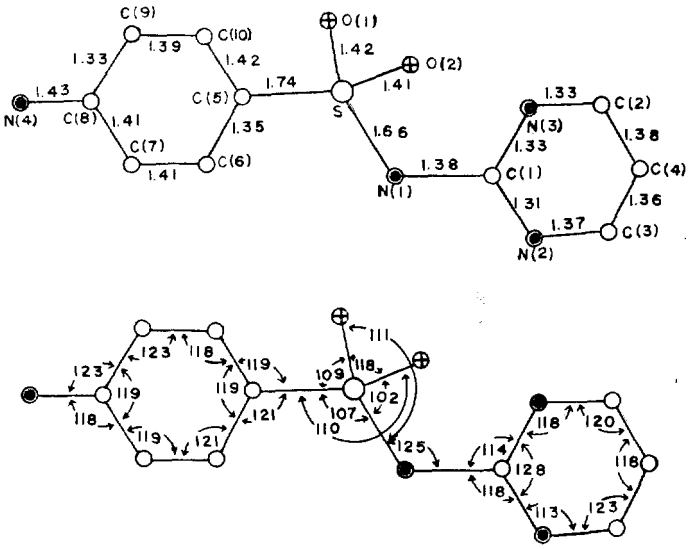

Fig. 1. Interatomic distances(Å) and bond angles(°)

The S—C(5) bond distance, 1.74(2) Å, is in good agreement with the theoretical S—C(sp^2) value (1.75 Å) calculated from the atomic radii and electronegativities given by Truter[10] and with the experimental data obtained for sulfanilamides[11~14]

The S—O bond distances, 1.41(2) and 1.42(2) Å, are in agreement with the values in the following reported structures; 1.42(1) and 1.43(1) Å in sulfaguanidine monohydrate[3], 1.440(6) and 1.434(10) Å in sulfathiazole[1,2], 1.430(8) and and 1.

Table 4. Least-squares planes in sulfadiazine. Equation for plane: $Ax+By+Cz=D$, where x, y, z are in Å.

Atoms in plane		Distance from best plane		Given constant
Benzene ring plane	C(5)	C(5)	+0.01 Å	A=0.584
	C(6)	C(6)	+0.01	B=0.333
	C(7)	C(7)	−0.01	C=0.422
	C(8)	C(8)	0.00	D=4.962
	C(9)	C(9)	+0.02	
	C(10)	C(10)	−0.02	
		S	0.00	
		N(1)	+1.38	
		N(4)	0.00	
Pyrimidine ring plane	N(2)	N(2)	0.00 Å	A=0.182
	N(3)	N(3)	+0.01	B=0.624
	C(1)	C(1)	0.00	C=−0.765
	C(2)	C(2)	−0.01	D=−4.59
	C(3)	C(3)	+0.01	
	C(4)	C(4)	0.00	
		S	+0.42	
		N(1)	+0.02	

435 (8) Å in *S,S*-diphenyl-*N*-*p*-toylsulfonyl sulfilimine[15].

The S—N(1) bond distance, 1.66 (2) Å, is in agreement with the values of the other sulfur compounds[1,2,3,15].

Tetrahedral geometry about the sulfur atom is demonstrated by the six bond angles O(1)—S—C(5) (109°), O(2)—S—C(5) (110°), O(1)—S—O(2) (118°), O(1)—S—N(1) (111°), O(2)—S—N(1) (102°) and C(5)—S—N(1) (107°). The atoms around the sulfur atom are arranged in a slightly distorted tetrahedral configuration.

The average values of C—N and C—C bond distances within the pyrimidine ring are 1.33 and 1.37 Å, respectively. The angles at the nitrogen atoms are less than 120° and the an-

Table 5. Intermolecular contacts.

Symmetry code					
	x	,	y	,	z
a	x	,	$1/2-y$	,	$-1/2+z$
b	x	,	$-1/2-y$	,	$-1/2+z$
b	$1-x$	,	$-y$	,	$1-z$
d	$1-x$	,	$1-y$	,	$1-z$
Hydrogen bonds					
O(1)·····H—N(4a)					2.96 Å
O(2)·····H—N(4b)					2.95
N(1)—H·····N(3c)					2.92
Other contacts less than 3.4 Å					
O(1)·····C(2d)					3.30 Å
O(2)·····C(2c)					3.28

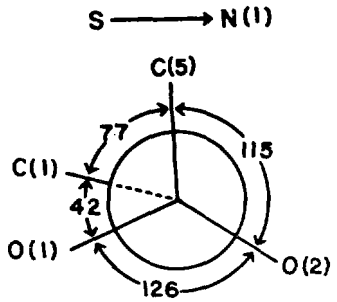

Fig. 2. Newman projection down the S—N(1) bond in sulfadiazine showing the conformation angles in degrees.

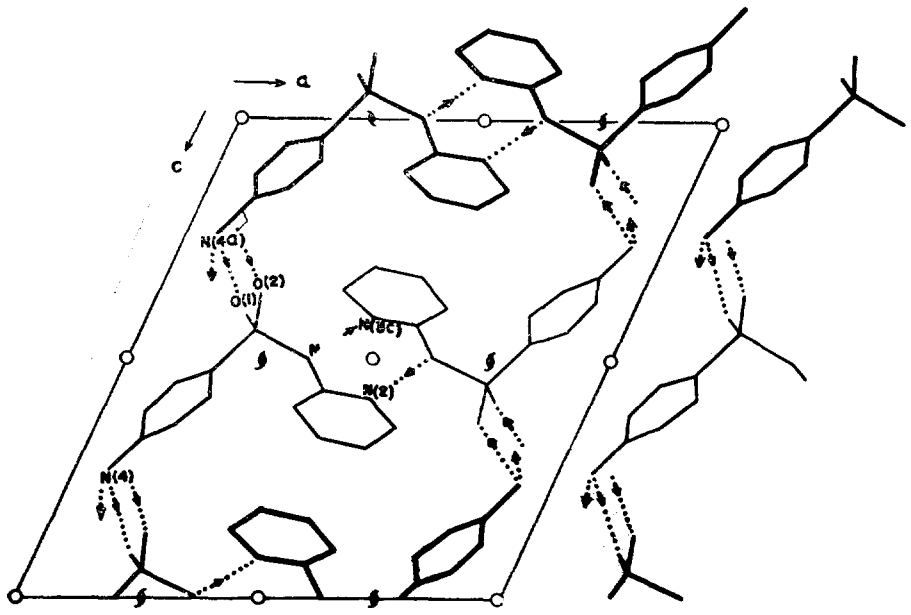

Fig. 3. Projection of the crystal structure of sulfadiazine along the *b* axis. Dotted lines are hydrogen bonds.

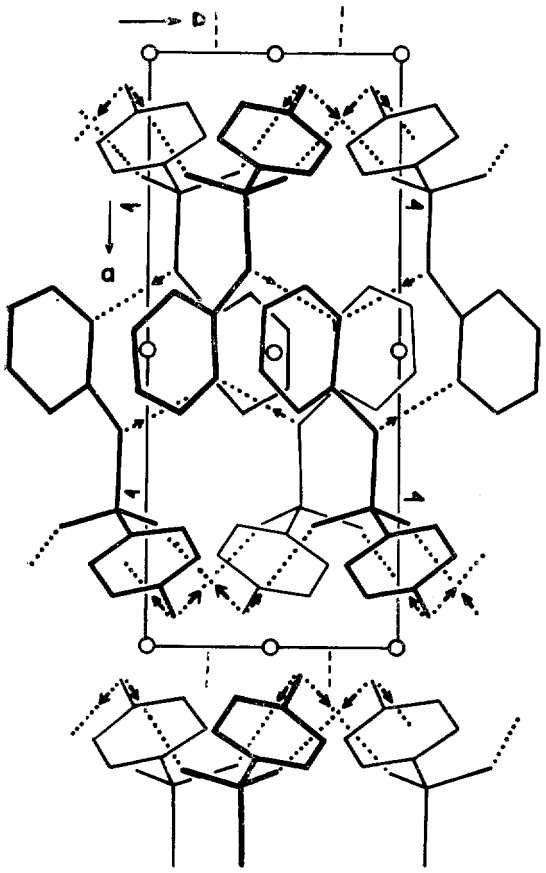

Fig. 4. Projection of the crystal structure of sulfadiazine along the *c* axis. Dotted lines are hydrogen bonds.

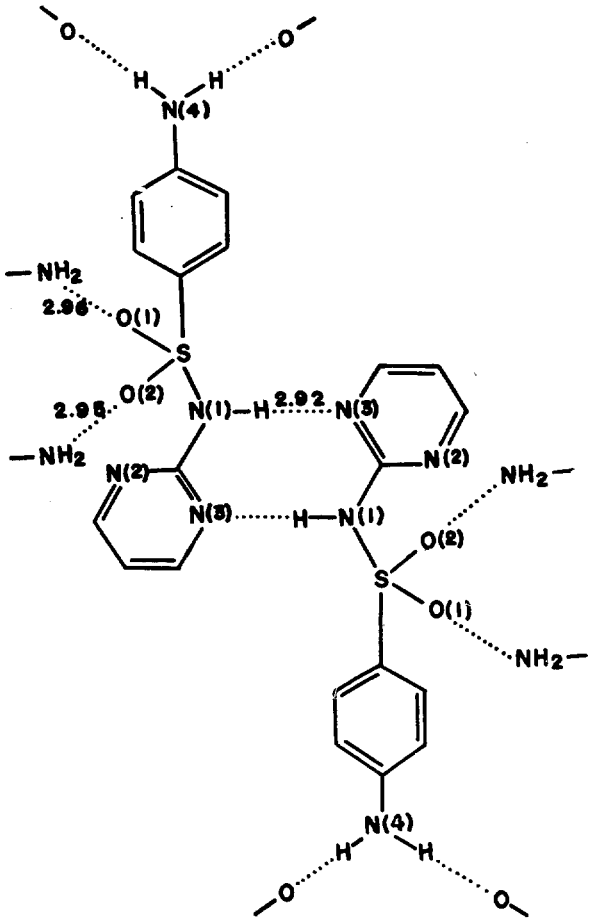

Fig. 5. The hydrogen bonding in sulfadiazine.

gles at the carbon atoms are all greater than 120° with the exception of that at C(4), which is 118°. These results are well agreement with those found in the structure of *syn*-4-pyrimidine carboxaldehyde oxime[16].

Table 4 gives the results of least-squares planes of the two rings in the molecule. The benzene ring is planar and is turned at an angle of 76° to the plane of the pyrimidine ring, which is also planar.

The molecular conformation around the S—N (1) bond is shown in *Fig.* 2. It is seen that the S—C(5) bond is gauche with 77° to N(1) —C(1) bond.

The contacts which could be considered as hydrogen bonds and other intermolecular contacts less than 3.4 Å are listed in *Table* 5.

Projection diagrams illustrating the molecular packing of sulfadiazine are shown in *Fig.* 3 and 4.

The structure is stabilized by a two dimensional network of hydrogen bonds. Although hydrogen atoms were not located in the present study, there are three hydrogen atoms available for hydrogen bond formation.

Amino group forms two hydrogen bonds, one

of distance 2.96 Å from atom O(1) to atom N ($4a$), and the other of distance 2.95 Å from atom O(2) to atom N($4b$).

The imino nitrogen atom, N(1), and pyrimidine nitrogen atom, N($3c$), form intermolecular N(1)—H···N($3c$) hydrogen bonds between the two molecules related by center of symmetry. The hydrogen bonding scheme in sulfadiazine is very similar to that of sulfathiazole *I*[2]. Thus the molecules are arranged in infinite strings along the b and c axial directions by means of intermolecular hydrogen bonds and the interlayer force appears to be van der Waals in character.

The oxygen atoms, O(1) and O(2), are involved in the shortest intermolecular contacts of 3.28 and 3.30 Å, respectively. That is, the intermolecular distances O(1)···C($2d$) and O(2)···C($2c$) are somewhat shorter than the sum of the corresponding van der Waals radii.

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