

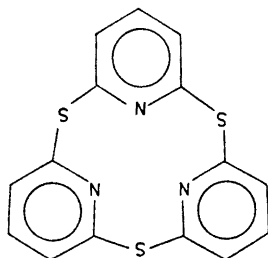
Crystal Structure of a Cyclisation Product of 6-Chloropyridid-2-thione ($C_{15}H_9N_3S_3$)

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The crystals are monoclinic with space group $P2_1/c$, cell dimensions $a = 14.21$, Å, $b = 7.88$, Å, $c = 15.20$, Å, $\beta = 119.5^\circ$, and four molecules in the unit cell. The structure was solved by direct methods and refined by full-matrix least squares technique to an R -value of 2.8 % ($R_w = 3.4$ %) for 1115 reflections recorded on an automatic four circle diffractometer. The molecule has a pseudo mirror plane and the angles between the three ring planes are 66° , 61° and 57° . Average bond distances and angles are: C-S: 1.780 Å, C-N: 1.335 Å, C-C: 1.376 Å, C-S-C: 101.9° , N-C-S: 117.7° , C-C-S: 118.7° , C-N-C: 116.7° , N-C-C: 123.5° , C-C-C: 118.6° with estimated standard deviations of about 0.005 Å and 0.4° in the individual values. The average N-N distance across the ring is 2.941 Å.

Intermolecular reactions of 6-chloropyridid-2-thione have recently been studied by Reistad *et al.*¹ Such reactions will eventually lead to polymerization or to cyclisation at some intermediate stage. NMR evidence for the simplest product is in favour of a cyclic trimeric pyridine with sulphur bridges between the pyridyl 2,6-positions.



In order to obtain conformational information of this new 12-membered heterocyclic ring system a crystal structure determination has been carried out.

The crystals are monoclinic with space group $P2_1/c$. The cell dimensions, determined by a manual four circle diffractometer, with estimated standard

deviations ^{2*} are: $a = 14.217(3)$ Å, $b = 7.885(2)$ Å, $c = 15.207(5)$ Å, $\beta = 119.57(2)^\circ$. The unit cell contains four molecules ($\rho_{\text{calc}} = 1.46$ g cm⁻³, $\rho_{\text{obs}} = 1.47$ g cm⁻³).

1300 reflections were measured on an automatic four circle diffractometer ($2\theta_{\text{max}} = 45^\circ$), using MoK α -radiation and a highly orientated graphite crystal monochromator. With an observed-unobserved cutoff at $2.0\sigma(I)$, 1115 reflections were recorded as observed. No corrections for absorption or secondary extinction effects have been carried out.

The structure was solved by direct methods and refined by full-matrix least squares technique.

Anisotropic temperature factors were introduced for sulphur, nitrogen, and carbon atoms. For hydrogens only positional parameters (having been calculated) were refined. The weights in least squares were obtained from the standard deviations in intensities, $\sigma(I)$, taken as

$$\sigma(I) = [C_T + (0.02 C_N)^2]^\dagger$$

where C_T is the total number of counts, and C_N the net count (peak minus background). The R -value arrived at was 2.8 % (weighted value $R_w = 3.4$ %) for 1115 observed reflections. The atomic form factors were those of Hanson *et al.*³ except for hydrogen.⁴

Final fractional coordinates and thermal parameters with estimated standard deviations are given in Tables 1 and 2. The expression for anisotropic vibration is:

$$\exp [- (B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{22}kl)]$$

Table 1. Fractional atomic coordinates and anisotropic thermal vibration parameters with estimated standard deviations (multiplied by 10⁵).*

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S ₁	14407 8	68376 16	18260 8	1022 11	4257 37	794 9	1418 33	1082 17	1684 29
S ₂	20921 6	48265 11	54471 6	704 8	1988 21	545 6	267 22	650 11	-21 19
S ₃	40562 9	16562 13	36908 9	1289 12	1931 24	1575 13	692 27	2131 22	34 28
N ₁	16404 18	59795 33	36173 18	611 24	1870 62	625 21	265 62	659 39	187 60
N ₂	30400 19	30038 31	46072 19	615 63	1608 60	738 22	170 62	673 39	103 61
N ₃	28874 20	43904 35	27637 19	640 24	223 67	701 21	-251 67	835 39	-391 63
C ₁	09831 25	66260 43	27113 24	698 31	1926 80	651 27	259 81	656 50	318 74

* All programs used are included in this reference.

Table 1. Continued.

C ₂	-00542	71849	24175	686	2292	744	656	515	648
	29	47	30	30	91	27	87	50	84
C ₃	-04227	70658	30919	619	2509	1010	816	765	610
	29	48	30	31	95	35	91	59	94
C ₄	02298	63329	40171	664	2102	893	356	967	125
	26	45	28	32	83	31	86	55	87
C ₅	12441	57942	42456	601	1428	625	-85	614	-158
	23	39	22	28	66	26	71	46	67
C ₆	24538	28969	50687	549	1711	495	27	408	100
	24	39	21	27	76	23	77	43	68
C ₇	21353	13827	52978	1286	1971	817	-130	1323	359
	32	48	27	42	86	31	100	63	87
C ₈	24332	-00934	50175	1788	1730	1071	-192	1814	243
	39	52	33	52	86	36	113	75	91
C ₉	29948	-00204	45040	1424	1308	1018	232	1281	100
	34	45	30	45	76	35	100	67	87
C ₁₀	32744	15539	43065	785	1607	741	320	750	-99
	26	43	24	32	76	27	82	51	75
C ₁₁	38897	38065	33014	719	2148	787	-82	965	-475
	26	43	25	32	86	29	87	54	82
C ₁₂	47976	47690	35451	630	3087	1015	-88	817	478
	29	58	30	32	110	34	101	57	101
C ₁₃	46588	63945	32083	719	3514	944	-1200	502	440
	33	61	32	35	123	34	114	59	112
C ₁₃	36444	70663	26985	1209	2024	738	-765	964	-32
	34	51	28	42	89	30	101	64	81
C ₁₄	27814	60284	25057	926	1948	535	-39	871	-143
	27	45	22	36	78	31	93	59	87

* For numbering of atoms, see Fig. 1.

A comparison between observed and calculated structure factors is presented in Table 3.

The principal axes of the thermal vibration ellipsoids were calculated from the thermal parameters of Table 1. Root mean square amplitudes and the corresponding *B*-values for the atomic anisotropic thermal vibration along the principal axes together with the components of these axes along the crystal ones are given in Table 4.

Rigid body analysis of translational, librational, and screw motion⁵ gave relatively large r.m.s. discrepancy between atomic vibration tensor components calculated from the thermal parameters of Table 1 and those calculated from the rigid body parameters. By including all non-hydrogen

Table 2. Fractional atomic coordinates with e.s.d.'s for hydrogen atoms. The isotropic thermal parameter is 5.0 \AA^2 for all.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
H ₂	-.0472 23	-.7700 37	-1.802 23
H ₃	-.1173 25	-.7493 38	-.2852 21
H ₄	-.0008 23	-.6256 38	-.4507 21
H ₇	-.1671 22	-.1411 36	-.5651 21
H ₈	-.2222 22	-.1243 40	-.5189 20
H ₉	-.3213 22	-.1013 39	-.4307 20
H ₁₂	-.5466 23	-.4308 37	-.3929 21
H ₁₃	-.5285 25	-.7030 37	-.3381 22
H ₁₄	-.3505 23	-.8245 39	-.2516 21

atoms the value obtained was 0.010 \AA^2 , which by no means supports the assumption of regarding the molecule as an oscillating rigid body. The coordinates were therefore not corrected for librational motion.

Bond distances and angles and dihedral angles are listed in Tables 5 and 6. The C-S bond lengths, in the range $1.769 \text{ \AA} - 1.790 \text{ \AA}$, are not far from a single bond (1.816 \AA).⁶ The fact that there is little conjugation between the pyridine rings through the sulphur bridges is also indicated by the UV spectra.¹ Similar results have been reported for diphenyl sulphides.⁷ As indicated in Fig. 2, the molecule has a pseudo mirror plane through S₂, N₃, C₁₃. The more symmetrical form with a threefold axis of symmetry is thus not preferred. Repulsion between the lone pair electrons on the pyridyl nitrogens may possibly explain this since, in the latter case, the principal direction of all three orbitals would be towards a common point. The bond distances C-S₁ and C-S₃ seem to be somewhat shorter (mean value 1.774 \AA) than C-S₂ (1.789 \AA). Also the angle at S₂ (101.0°) is apparently significantly smaller than those at S₁ and S₃ (102.1°). However, in view of the fact that S₁ and S₃ (but not S₂) have very large thermal vibration amplitudes (see Table 4), the significance of these differences may be doubted.

Table 4. Continued.

N ₁	.127	.208	.150	.251	4.99
	.046	-.105	.223	.230	4.16
	.211	-.067	.033	.208	3.40
N ₂	.081	.030	.287	.259	5.28
	.124	.196	.007	.230	4.17
	.203	-.107	.063	.210	3.48
N ₃	.117	-.228	.182	.279	6.13
	.151	.136	.216	.236	4.39
	-.171	.006	.048	.199	3.12
C ₁	.114	.201	.189	.260	5.35
	.155	.057	-.110	.237	4.43
	.186	-.130	.169	.222	3.88
C ₂	.086	.218	.226	.294	6.83
	.165	.118	-.118	.272	5.86
	.189	-.104	.150	.202	3.23
C ₃	.124	.174	.305	.318	8.01
	.088	.205	-.136	.283	6.34
	.201	-.082	.080	.194	2.96
C ₄	.178	.078	.312	.283	6.33
	.028	.239	-.087	.260	5.34
	-.188	.057	.001	.197	3.06
C ₅	.082	-.076	.256	.239	4.52
	.211	-.071	.018	.214	3.63
	.102	.185	.086	.208	3.42
C ₆	-.095	.153	.115	.237	4.45
	.123	.172	-.046	.229	4.16
	.189	-.031	.207	.202	3.22
C ₇	.361	-.012	.220	.317	7.94
	-.016	.212	.157	.269	5.70
	.031	.130	-.150	.213	3.57
C ₈	.427	-.016	.251	.373	11.01
	-.025	.120	.236	.276	6.02
	.022	.200	-.084	.222	3.89
C ₉	.381	.027	.167	.333	8.75
	.022	.001	.302	.292	6.75
	.019	-.201	.009	.202	3.22
C ₁₀	.092	.121	-.175	.264	5.49
	.248	.065	.236	.253	5.03
	-.101	.178	.016	.210	3.47
C ₁₁	.132	-.190	.244	.285	6.42
	.189	.167	.165	.245	4.63
	-.143	.060	.074	.200	3.16

	.035	.251	.233	.332	8.72
C_{12}	.095	-.183	.249	.284	6.38
	.233	.026	.056	.213	3.57
	-.132	.290	.154	.381	11.47
C_{13}	.107	-.137	.283	.283	6.34
	.212	.089	.083	.205	3.33
	.320	-.145	.074	.325	8.34
C_{14}	.124	.082	.276	.254	5.10
	.077	.190	-.068	.227	4.08
	.306	-.028	.161	.268	5.67
C_{15}	.031	.244	-.024	.249	4.88
	-.004	.031	.190	.195	3.00

Table 5. Bond distances and angles with e.s.d.'s. (For numbering of atoms, see Fig. 1. H_n is bonded to C_n .)

Distance	Å	Distance	Å
S_3-C_1	1.769(3)	C_6-C_7	1.381(4)
S_1-C_{16}	1.778(4)	C_7-C_8	1.376(5)
S_2-C_5	1.788(3)	C_8-C_9	1.366(5)
S_2-C_5	1.790(3)	C_9-C_{10}	1.381(4)
S_3-C_{10}	1.774(4)	$C_{11}-C_{12}$	1.380(5)
S_2-C_{11}	1.773(4)	$C_{12}-C_{13}$	1.358(5)
N_1-C_1	1.327(4)	$C_{13}-C_{14}$	1.363(5)
N_1-C_5	1.336(4)	$C_{14}-C_{15}$	1.381(5)
N_2-C_6	1.331(4)	C_2-H_2	0.92(3)
N_2-C_{10}	1.333(4)	C_3-H_3	1.00(3)
N_3-C_{11}	1.327(4)	C_4-H_4	0.94(3)
N_3-C_{15}	1.337(4)	C_7-H_7	1.04(3)
C_1-C_2	1.385(5)	C_8-H_8	1.03(3)
C_2-C_3	1.366(5)	C_9-H_9	0.94(3)
C_5-C_4	1.373(5)	$C_{12}-H_{12}$	0.91(3)
C_4-C_5	1.373(4)	$C_{13}-C_{13}$	0.94(3)
		$C_{14}-C_{14}$	0.96(3)
Angle	(°)	Angle	(°)
$C_1-S_1-C_{16}$	102.4(1)	$C_2-C_3-C_4$	118.9(3)
$C_5-S_2-C_6$	101.0(2)	$C_3-C_4-C_5$	118.9(3)
$C_{10}-S_2-C_{11}$	101.8(2)	$C_6-C_7-C_8$	117.6(3)
$N_1-C_1-S_1$	119.4(2)	$C_7-C_8-C_9$	119.8(4)
$N_1-C_5-S_2$	117.9(2)	$C_8-C_9-C_{10}$	118.3(4)
$N_2-C_6-S_2$	118.0(2)	$C_{11}-C_{12}-C_{13}$	118.4(4)
$N_2-C_{10}-S_2$	118.0(2)	$C_{13}-C_{13}-C_{14}$	119.8(4)
$N_3-C_{11}-S_1$	116.8(3)	$C_{13}-C_{14}-C_{15}$	118.0(4)
$N_3-C_{15}-S_3$	117.6(2)	$C_1-C_2-H_2$	121(2)
$C_2-C_1-S_1$	117.3(3)	$H_2-C_2-C_3$	120(2)
$C_4-C_5-S_2$	119.0(3)	$C_2-C_3-H_3$	116(2)
$C_7-C_8-S_2$	118.1(3)	$H_3-C_3-C_4$	125(2)
$C_9-C_{10}-S_2$	118.6(3)	$C_3-C_4-H_4$	121(2)

Table 5. Continued.

$C_{14}-C_{15}-S_1$	119.7(3)	$H_4-C_4-C_5$	120(2)
$C_{12}-C_{11}-S_3$	118.9(3)	$C_6-C_7-H_7$	119(2)
$C_1-N_1-C_5$	117.1(3)	$H_7-C_7-C_8$	123(2)
$C_6-N_2-C_{10}$	117.0(3)	$C_7-C_8-H_8$	120(2)
$C_{11}-N_3-C_{15}$	116.6(3)	$H_8-C_8-C_9$	121(2)
$N_1-C_1-C_3$	123.3(3)	$C_8-C_9-H_9$	121(2)
$N_1-C_5-C_4$	123.1(3)	$H_9-C_9-C_{10}$	120(2)
$N_2-C_6-C_7$	123.8(3)	$C_{11}-C_{12}-H_{12}$	120(2)
$N_2-C_{10}-C_9$	123.3(3)	$H_{12}-C_{12}-C_{13}$	122(2)
$N_3-C_{11}-C_{12}$	123.5(3)	$C_{12}-C_{13}-H_{13}$	117(2)
$N_3-C_{15}-C_{14}$	123.4(3)	$H_{13}-C_{13}-C_{14}$	123(2)
$C_1-C_2-C_3$	118.6(3)	$C_{13}-C_{14}-H_{14}$	123(2)
		$H_{14}-C_{14}-C_{15}$	118(2)

Each of the three 2,6-sulphursubstituted pyridyl groups are planar to within 0.05 Å. The angles between these planes (Fig. 2) are:

$$\angle I,II : 66.3^\circ, \angle I,III : 61.0^\circ, \angle II,III : 57.1^\circ.$$

The average bond distances and angles of the pyridine rings agree within probable limits of error with the micro wave results for pyridine:⁸

	Title compound	Pyridine
C-N	1.335 Å	1.3402 Å
C-C	1.376 Å	1.3945 Å
C-N-C	116.7°	116° 50'
N-C-C	123.5°	123° 53'
C-C-C	118.6°	118° 26'

In fact the C-C distances seem to be somewhat shorter than the pyridine value. However, from Table 4 may be seen that the carbon atoms C_2 , C_3 , C_4 , C_7 , C_8 , C_9 , C_{12} , C_{13} and C_{14} have relatively large thermal vibration amplitudes (in the range 6.3 Å to 11.5 Å). Since no corrections in positional parameters

Table 6. Some dihedral angles with e.s.d.'s.

Angle	(°)
$N_3-C_{15}-S_1-C_1$	64.1 (3)
$N_1-C_1-S_1-C_{15}$	0.0 (3)
$N_3-C_{11}-S_3-C_{10}$	53.5 (3)
$N_2-C_{10}-S_2-C_{11}$	19.1 (3)
$N_1-C_5-S_2-S_3$	53.5 (3)
$N_2-C_6-S_2-C_5$	64.5 (3)

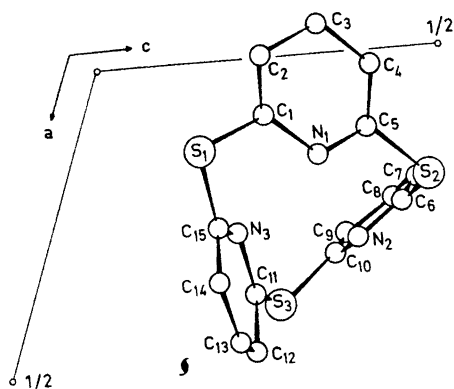


Fig. 1. Schematic drawing of the molecule viewed along [010].

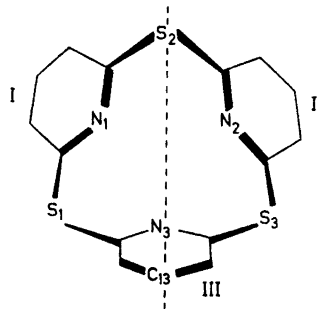


Fig. 2.

for this motion have been made, the difference cannot with confidence be regarded as significant.

The N—N distances across the ring correspond to van der Waals contacts:

$$N_1 \cdots N_2: 2.962 \text{ \AA}; N_1 \cdots N_3: 2.945 \text{ \AA}; N_2 \cdots N_3: 2.916 \text{ \AA}.$$

No short *intermolecular* distances have been found.

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