

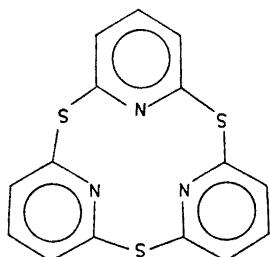
Crystal Structure of a Cyclisation Product of 6-Chloropyrid-2-thione ($C_{15}H_9N_3S_3$)

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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-chloropyrid-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

$$\sigma(I) = [C_T + (0.02 C_N)^2]^{1/2}$$

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:

$$\exp [- (B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$$

Table 1. Fractional atomic coordinates and anisotropic thermal vibration parameters with estimated standard deviations (multiplied by 10^5).*

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | 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 29 | 71849 47 | 24175 30 | 686 30 | 2292 91 | 744 27 | 656 87 | 515 50 | 648 84 |
| C ₃ | -04227 29 | 70658 48 | 30919 30 | 619 31 | 2509 95 | 1010 35 | 816 91 | 765 59 | 610 94 |
| C ₄ | 02298 26 | 63329 45 | 40171 28 | 664 32 | 2102 83 | 893 31 | 356 86 | 967 55 | 125 87 |
| C ₅ | 12441 23 | 57942 39 | 42456 22 | 601 28 | 1428 66 | 625 26 | -85 71 | 614 46 | -158 67 |
| C ₆ | 24538 24 | 28969 39 | 50687 21 | 549 27 | 1711 76 | 495 23 | 27 77 | 408 43 | 100 68 |
| C ₇ | 21353 32 | 13827 48 | 52978 27 | 1286 42 | 1971 86 | 817 31 | -130 100 | 1323 63 | 359 87 |
| C ₈ | 24332 39 | -00934 52 | 50175 33 | 1788 52 | 1730 86 | 1071 36 | -192 113 | 1814 75 | 243 91 |
| C ₉ | 29948 34 | -00204 45 | 45040 30 | 1424 45 | 1308 76 | 1018 35 | 232 100 | 1281 67 | 100 87 |
| C ₁₀ | 32744 26 | 15539 43 | 43065 24 | 785 32 | 1607 76 | 741 27 | 320 82 | 750 51 | -99 75 |
| C ₁₁ | 38897 26 | 38065 43 | 33014 25 | 719 32 | 2148 86 | 787 29 | -82 87 | 965 54 | -475 82 |
| C ₁₂ | 47976 29 | 47690 58 | 35451 30 | 630 32 | 3087 110 | 1015 34 | -88 101 | 817 57 | 478 101 |
| C ₁₃ | 46588 33 | 63945 61 | 32083 32 | 719 35 | 3514 123 | 944 34 | -1200 114 | 502 59 | 440 112 |
| C ₁₄ | 36444 34 | 70663 51 | 26985 28 | 1209 42 | 2024 89 | 738 30 | -765 101 | 964 64 | -32 81 |
| C ₁₄ | 27814 27 | 60284 45 | 25057 22 | 926 36 | 1948 78 | 535 31 | -39 93 | 871 59 | -143 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 Å² for all.

| Atom | <i>x</i> | <i>y</i> | <i>z</i> |
|-----------------|--------------|--------------|--------------|
| H ₂ | -.0472 23 | -.7700 37 | -.1802 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 Å², 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 Å–1.790 Å, are not far from a single bond (1.816 Å).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 Å) than C–S₂ (1.789 Å). 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 3. Continued.

| h | k | l | Fo | Fc | h | k | l | Fo | Fc | h | k | l | Fo | Fc | h | k | l | Fo | Fc |
|----------|----------|----------|-----------|-----------|----------|----------|----------|-----------|-----------|----------|----------|----------|-----------|-----------|----------|----------|----------|-----------|-----------|
| 11 | 3 | -2 | 290 | 245 | 3 | 6 | 3 | 116 | 120 | 8 | -8 | 91 | 97 | 2 | 5 | -1 | 250 | 8 | 401 |
| 11 | 3 | -1 | 110 | -1 | 3 | 4 | 4 | 123 | 128 | 8 | -7 | 261 | -2 | 3 | 5 | -1 | 325 | 8 | 455 |
| 12 | 3 | -9 | 149 | 142 | 3 | 4 | 5 | 196 | 192 | 8 | -6 | 248 | -3 | 1 | 2 | 0 | 321 | 8 | 545 |
| 12 | 3 | -7 | 173 | -178 | 3 | 4 | 6 | 199 | 193 | 7 | -1 | 239 | -1 | 1 | 1 | 1 | 116 | 8 | 544 |
| 12 | 3 | -5 | 179 | -177 | 3 | 4 | 7 | 200 | -213 | 8 | -5 | 194 | -1 | 1 | 2 | -1 | 112 | 8 | 543 |
| 12 | 3 | -4 | 219 | -216 | 3 | 4 | 8 | 209 | -215 | 8 | -4 | 190 | -2 | 0 | 2 | 0 | 210 | 9 | 510 |
| 12 | 3 | -3 | 101 | -92 | 4 | -4 | -14 | 111 | 110 | 9 | -3 | 133 | 135 | 5 | 5 | 5 | 119 | 9 | 59 |
| 13 | 3 | -5 | 130 | -124 | 4 | -4 | -13 | 86 | -86 | 9 | -2 | 137 | 142 | 3 | 3 | -1 | 126 | 9 | 58 |
| 13 | 3 | -4 | 164 | -165 | 4 | -4 | -12 | 86 | -86 | 9 | -1 | 131 | 137 | 3 | 3 | -1 | 126 | 9 | 57 |
| 13 | 3 | -3 | 165 | -164 | 4 | -4 | -10 | 223 | -217 | 9 | -1 | 219 | -2 | 5 | 3 | -1 | 211 | 9 | 56 |
| 6 | 4 | -12 | 135 | -132 | 4 | -9 | -40 | -92 | 9 | -7 | 101 | 1 | 4 | 3 | 5 | -5 | 191 | 9 | 55 |
| 6 | 4 | -9 | 103 | 110 | 4 | -8 | -157 | -152 | 9 | -1 | 142 | 1 | 8 | 3 | 5 | -1 | 194 | 9 | 54 |
| 6 | 4 | -6 | 78 | -76 | 4 | -8 | -156 | -155 | 9 | -1 | 143 | 1 | 8 | 3 | 5 | -1 | 193 | 9 | 53 |
| 6 | 4 | -3 | 256 | -257 | 4 | -5 | -135 | -127 | 10 | -4 | 113 | 147 | 3 | 3 | -2 | 189 | 7 | 52 | |
| 6 | 4 | -1 | 463 | 455 | 4 | -4 | -134 | -138 | 10 | -4 | 112 | 141 | 1 | 1 | 1 | 150 | 7 | 51 | |
| 6 | 4 | -1 | 335 | 311 | 4 | -3 | -93 | -90 | 74 | 0 | 112 | 143 | 3 | 5 | 9 | 145 | 7 | 50 | |
| 6 | 4 | -1 | 331 | 310 | 4 | -3 | -93 | -90 | 74 | 0 | 112 | 143 | 3 | 5 | 9 | 145 | 7 | 49 | |
| 6 | 4 | -1 | 624 | -621 | 4 | -3 | -776 | -742 | 10 | -8 | 144 | -2 | 1 | 3 | 3 | -205 | 6 | 48 | |
| 6 | 4 | -1 | 106 | -94 | 4 | -3 | 452 | -451 | 10 | -7 | 195 | 198 | 3 | 5 | 5 | 217 | 6 | 47 | |
| 6 | 4 | -1 | 616 | -611 | 4 | -2 | 266 | -260 | 10 | -5 | 216 | 212 | 4 | 5 | -9 | 343 | 6 | 46 | |
| 6 | 4 | -1 | 339 | -320 | 4 | -3 | 122 | -130 | 10 | -4 | 224 | 222 | 4 | 5 | -1 | 206 | 6 | 45 | |
| 6 | 4 | -1 | 329 | -311 | 4 | -2 | 127 | -129 | 10 | -4 | 224 | 221 | 4 | 5 | -1 | 206 | 6 | 44 | |
| 6 | 4 | -1 | 305 | -291 | 4 | -2 | 128 | -129 | 10 | -4 | 224 | 221 | 4 | 5 | -1 | 206 | 6 | 43 | |
| 6 | 4 | -1 | 250 | -257 | 5 | -4 | -12 | 104 | -111 | 4 | -5 | 275 | -271 | 4 | 5 | -3 | 311 | 7 | 77 |
| 6 | 4 | -1 | 78 | -88 | 5 | -4 | -126 | 121 | 11 | -3 | 275 | -271 | 4 | 5 | -3 | 311 | 7 | 76 | |
| 6 | 4 | -1 | 170 | -188 | 5 | -4 | -127 | 121 | 11 | -3 | 276 | -271 | 4 | 5 | -3 | 311 | 7 | 75 | |
| 6 | 4 | -1 | 134 | -122 | 5 | -4 | -64 | -87 | 12 | -4 | 113 | 184 | 1 | 1 | -1 | 224 | 7 | 74 | |
| 6 | 4 | -1 | 142 | -127 | 5 | -4 | -53 | 134 | 121 | 12 | -4 | 113 | 193 | 4 | 5 | 1 | 227 | 7 | 73 |
| 1 | 4 | -11 | 115 | -122 | 5 | -4 | -44 | 355 | 355 | 12 | -4 | 176 | -199 | 4 | 5 | 358 | 315 | 1 | 6 |
| 1 | 4 | -4 | 114 | 111 | 5 | -4 | -2 | 135 | 135 | 12 | -4 | 176 | -199 | 4 | 5 | 358 | 315 | 1 | 5 |
| 1 | 4 | -3 | 111 | 112 | 5 | -4 | -1 | 136 | 136 | 12 | -4 | 177 | -199 | 4 | 5 | 358 | 315 | 1 | 4 |
| 1 | 4 | -2 | 149 | 145 | 5 | -4 | -1 | 161 | 169 | 0 | -5 | 110 | 86 | 4 | 5 | 92 | 91 | 1 | 3 |
| 1 | 4 | -1 | 51 | 58 | 5 | -1 | 70 | 68 | 0 | -5 | 149 | 156 | 4 | 5 | -10 | 115 | 1 | 2 | |
| 1 | 4 | -1 | 167 | 164 | 5 | -1 | 82 | 98 | 0 | -5 | 195 | 192 | 5 | 5 | -8 | 172 | 1 | 1 | |
| 1 | 4 | -2 | 394 | 418 | 5 | -4 | -127 | 124 | 9 | -3 | 364 | 359 | 5 | 5 | -7 | 108 | 6 | 96 | |
| 1 | 4 | -3 | 301 | 327 | 5 | -4 | -86 | 80 | 0 | -5 | 256 | 255 | 5 | 5 | -5 | 167 | 7 | 95 | |
| 1 | 4 | -5 | 162 | 177 | 5 | -4 | -117 | 116 | 0 | -5 | 262 | 255 | 5 | 5 | -3 | 113 | 7 | 94 | |
| 1 | 4 | -9 | 176 | 174 | 5 | -4 | -122 | 93 | 0 | -5 | 349 | 349 | 5 | 5 | -3 | 107 | 7 | 93 | |
| 1 | 4 | -11 | 111 | 111 | 5 | -4 | -99 | 111 | 0 | -5 | 174 | 174 | 1 | 1 | 2 | 205 | 7 | 92 | |
| 1 | 4 | -11 | 110 | 112 | 5 | -4 | -10 | 76 | 0 | -5 | 174 | 174 | 1 | 1 | 2 | 205 | 7 | 91 | |
| 1 | 4 | -11 | 113 | 112 | 5 | -4 | -10 | 76 | 1 | -2 | 205 | 205 | 1 | 1 | 2 | 205 | 7 | 90 | |
| 1 | 4 | -11 | 116 | 111 | 5 | -4 | -10 | 366 | 357 | 0 | -5 | 161 | 153 | 5 | 5 | -1 | 216 | 7 | 89 |
| 1 | 4 | -10 | 116 | 114 | 5 | -4 | -10 | 263 | 257 | 0 | -5 | 163 | 155 | 5 | 5 | -1 | 216 | 7 | 88 |
| 1 | 4 | -10 | 164 | 164 | 5 | -4 | -5 | 63 | 71 | 0 | -5 | 95 | 95 | 5 | 5 | -2 | 114 | 7 | 87 |
| 1 | 4 | -2 | 132 | 134 | 5 | -4 | -1 | 153 | 152 | 0 | -5 | 111 | 117 | 5 | 5 | -3 | 219 | 2 | 86 |
| 1 | 4 | -4 | 72 | 74 | 5 | -4 | -3 | 43 | 43 | 1 | -5 | 104 | 115 | 5 | 5 | -3 | 179 | 7 | 85 |
| 1 | 4 | -3 | 65 | 652 | 5 | -4 | -1 | 219 | 209 | 0 | -5 | 120 | 126 | 5 | 5 | -7 | 343 | 7 | 84 |
| 1 | 4 | -1 | 453 | 455 | 6 | -1 | 231 | 228 | 1 | -5 | 98 | 96 | 5 | 5 | -6 | 321 | 3 | 83 | |
| 2 | 4 | -1 | 58 | 67 | 6 | -1 | 362 | 368 | 1 | -5 | 170 | 169 | 6 | 5 | -5 | 63 | 3 | 82 | |
| 2 | 4 | -3 | 395 | 315 | 6 | -4 | 3 | 172 | 129 | 1 | -5 | 219 | 215 | 6 | 5 | -4 | 153 | 3 | 81 |
| 2 | 4 | -1 | 459 | 470 | 6 | -4 | 161 | 174 | 1 | -5 | 244 | 246 | 6 | 5 | -2 | 210 | 3 | 80 | |
| 2 | 4 | -3 | 329 | 328 | 7 | -1 | 173 | 178 | 1 | -5 | 165 | 166 | 5 | 0 | -1 | 97 | 3 | 79 | |
| 2 | 4 | -3 | 349 | 317 | 7 | -1 | 166 | 92 | 0 | -5 | 140 | 140 | 6 | 5 | -1 | 112 | 3 | 78 | |
| 2 | 4 | -4 | 299 | 210 | 7 | -4 | -5 | 100 | 101 | 1 | -5 | 247 | 199 | 5 | 5 | -2 | 114 | 3 | 77 |
| 2 | 4 | -5 | 75 | 74 | 7 | -4 | -5 | 43 | 42 | 0 | -5 | 211 | 213 | 7 | 5 | -1 | 115 | 3 | 76 |
| 2 | 4 | -1 | 141 | 143 | 7 | -4 | -3 | 149 | 176 | 1 | -5 | 174 | 176 | 7 | 5 | -6 | 149 | 3 | 75 |
| 2 | 4 | -1 | 143 | 146 | 7 | -4 | -7 | 69 | 69 | 0 | -5 | 113 | 112 | 7 | 5 | -4 | 103 | 3 | 74 |
| 2 | 4 | -1 | 142 | 144 | 7 | -4 | -1 | 134 | 134 | 1 | -5 | 217 | 216 | 7 | 5 | -6 | 226 | 3 | 73 |
| 3 | 4 | -11 | 41 | 46 | 7 | -4 | -1 | 109 | 114 | 1 | -5 | 161 | 141 | 7 | 5 | -1 | 213 | 2 | 72 |
| 3 | 4 | -7 | 54 | 55 | 7 | -4 | -2 | 100 | 116 | 0 | -5 | 126 | 124 | 7 | 5 | -3 | 145 | 2 | 71 |
| 3 | 4 | -5 | 155 | 110 | 7 | -4 | -3 | 122 | 117 | 0 | -5 | 149 | 149 | 5 | 5 | -2 | 231 | 2 | 70 |
| 3 | 4 | -4 | 65 | 71 | 7 | -4 | -1 | 113 | 120 | 0 | -5 | 166 | 166 | 5 | 5 | -3 | 145 | 2 | 69 |
| 3 | 4 | -1 | 150 | 178 | 7 | -4 | -13 | 98 | 97 | 0 | -5 | 195 | 195 | 5 | 5 | -3 | 154 | 2 | 68 |
| 3 | 4 | -1 | 151 | 149 | 7 | -4 | -10 | 165 | 165 | 0 | -5 | 212 | 211 | 5 | 5 | -2 | 231 | 2 | 67 |
| 3 | 4 | -2 | 246 | 273 | 8 | -4 | -9 | 318 | 315 | 2 | -5 | 63 | 61 | 5 | 6 | -7 | 143 | 1 | 66 |

Table 4. Continued.

| | | | | | |
|-----------------|-----------------------|------------------------|-----------------------|----------------------|-----------------------|
| N ₁ | .127 .046 .211 | .208 -.105 -.067 | .150 .223 .033 | .251 .230 .208 | 4.99 4.16 3.40 |
| N ₂ | .081 .124 .203 | .030 .196 -.107 | .287 .007 .063 | .259 .230 .210 | 5.28 4.17 3.48 |
| N ₃ | .117 .151 -.171 | -.228 .136 .006 | .182 .216 .048 | .279 .236 .199 | 6.13 4.39 3.12 |
| C ₁ | .114 .155 .186 | .201 .057 -.130 | .189 -.110 .169 | .260 .237 .222 | 5.35 4.43 3.88 |
| C ₂ | .086 .165 .189 | .218 .118 -.104 | .226 -.118 .150 | .294 .272 .202 | 6.83 5.86 3.23 |
| C ₃ | .124 .088 .201 | .174 .205 -.082 | .305 -.136 .080 | .318 .283 .194 | 8.01 6.34 2.96 |
| C ₄ | .178 .028 -.188 | .078 .239 .057 | .312 -.087 .001 | .283 .260 .197 | 6.33 5.34 3.06 |
| C ₅ | .082 .211 .102 | -.076 -.071 .185 | .256 .018 .086 | .239 .214 .208 | 4.52 3.63 3.42 |
| C ₆ | -.095 .123 .189 | .153 .172 -.031 | .115 -.046 .207 | .237 .229 .202 | 4.45 4.16 3.22 |
| C ₇ | .361 -.016 .031 | -.012 .212 .130 | .220 .157 -.150 | .317 .269 .213 | 7.94 5.70 3.57 |
| C ₈ | .427 -.025 .022 | -.016 .120 .200 | .251 .236 -.084 | .373 .276 .222 | 11.01 6.02 3.89 |
| C ₉ | .381 .022 .019 | .027 .001 -.201 | .167 .302 .009 | .333 .292 .202 | 8.75 6.75 3.22 |
| C ₁₀ | .092 .248 -.101 | .121 .065 .178 | -.175 .236 .016 | .264 .253 .210 | 5.49 5.03 3.47 |
| C ₁₁ | .132 .189 -.143 | -.190 .167 .060 | .244 .165 .074 | .285 .245 .200 | 6.42 4.63 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 ₄ —C ₁₅ | 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 ₆ | 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 ₃ —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 ₃ —C ₄ | 1.373(5) | C ₁₂ —H ₁₂ | 0.91(3) |
| C ₄ —C ₅ | 1.373(4) | C ₁₃ —C ₁₅ | 0.94(3) |
| | | C ₁₄ —C ₁₄ | 0.96(3) |

| Angle | (°) | Angle | (°) |
|--|----------|---|----------|
| C ₁ —S ₁ —C ₁₅ | 102.4(1) | C ₂ —C ₃ —C ₄ | 118.9(3) |
| C ₅ —S ₂ —C ₃ | 101.0(2) | C ₃ —C ₄ —C ₅ | 118.9(3) |
| C ₁₀ —S ₃ —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 ₃ | 118.0(2) | C ₁₂ —C ₁₃ —C ₁₄ | 119.8(4) |
| N ₃ —C ₁₅ —S ₁ | 116.8(3) | C ₁₃ —C ₁₄ —C ₁₅ | 118.0(4) |
| N ₃ —C ₁₁ —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 ₆ —S ₂ | 118.1(3) | H ₃ —C ₃ —C ₄ | 125(2) |
| C ₉ —C ₁₀ —S ₃ | 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) |
| $N_1-C_1-C_2$ | 123.3(3) | $C_8-C_9-H_9$ | 121(2) |
| $N_1-C_6-C_4$ | 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-sulphur-substituted 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) |
| $N_2-C_{10}-S_3-C_{11}$ | 19.1 (3) |
| $N_1-C_6-S_2-S_6$ | 53.5 (3) |
| $N_2-C_6-S_2-C_6$ | 64.5 (3) |

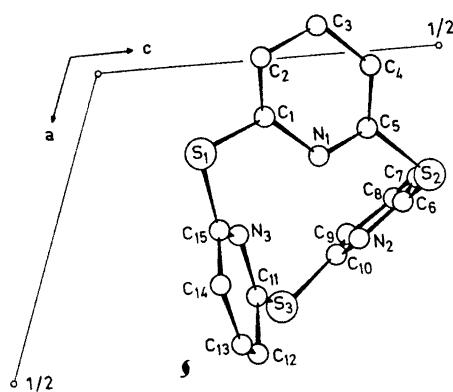


Fig. 1. Schematical drawing of the molecule viewed along [010].

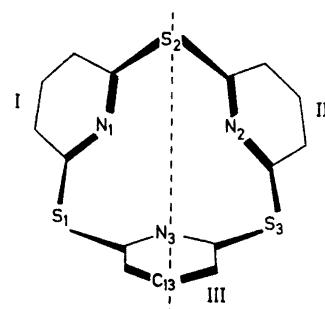


Fig. 2.

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:

N₁···N₂: 2.962 Å; N₁···N₃: 2.945 Å; N₂···N₃: 2.916 Å.

No short *intermolecular* distances have been found.

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