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References

- BASTIANSEN, O. & TRÆTTEBERG, M. (1962). *Tetrahedron*, **17**, 147–154.
- BORGEN, O., MESTVEDT, B. & FINJORD, J. (1969). Techn. Report 52, Institutt for Fysikalsk Kjemi, NTH.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757–758.
- CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896–897.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- EVENSEN, A. M. (1970). Thesis. Institutt for Røntgenteknikk, NTH.
- GOLDSTEIN, P., SEFF, K. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 778–791.
- KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **16**, 969–975.
- KJØSEN, H. & LIAAEN-JENSEN, S. (1970). *Acta Chem. Scand.* **24**, 2259–2260.
- LIDE, D. R. JR & MANN, D. E. (1958). *J. Chem. Phys.* **29**, 914–920.
- SHOEMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- STEWART, J. M., KRUGER, G. J., KUNDELL, F. A. & BALDWIN, J. C. (1971). The XRAY System, Version of Oct. 1971. Computer Science Center, Univ. of Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- SURMATHIS, J. D. & OFNER, A. (1963). *J. Chem. Soc.* **28**, 2735–2739.
- WITTIG, G. (1956). *Angew. Chem.* **68**, 505–508.

Acta Cryst. (1973). **B29**, 776

The Crystal and Molecular Structure of 3-Thioamidopyridine

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Crystals of 3-thioamidopyridine, $C_6H_6N_2S$, are monoclinic, space group $P2_1/n$ with four molecules in a unit cell of dimensions $a=4.004$, $b=10.572$ and $c=15.400$ Å, $\beta=96.42^\circ$. The crystal structure was solved by three-dimensional Patterson and Fourier syntheses using the heavy-atom technique. The atomic coordinates of all the atoms in the structure were initially refined by block-diagonal, least-squares calculations and completed by two cycles of full-matrix refinement. The final R index was 0.035 for 712 reflexions obtained from a Hilger-Watts four-circle automatic diffractometer using Mo $K\alpha$ radiation. The mean bond lengths in the pyridine ring are C–C = 1.378, C–N = 1.330 Å, with r.m.s. deviations of 0.005 and 0.006 Å respectively. The thioamido group has the dimensions C–C = 1.488, C–N = 1.307 and C–S = 1.666 Å with a mean e.s.d. of 0.005 Å. The locations of the amido hydrogen positions, together with the bond lengths and angles within the thioamido group, suggest a significant contribution from the ionic canonical form, as well as the amide form, to the overall electron arrangement within the thioamido group. The angle between the plane of the pyridine molecule and that of the thioamido group is 33.8° . Non-bonded contact radii of some atoms are proposed to interpret this interplanar angle. Two types of hydrogen bond have been found, one is of the type N–H...S (3.423 Å) and connects pairs of molecules across centres of symmetry and the other is of type N–H...N (2.955 Å) and connects pairs of molecules through the screw axis.

Introduction

The crystal and molecular structure of 3-thioamidopyridine is the third in a series of three isomeric thioamidopyridines of general formula $C_6H_6N_2S$, to be reported. In a previous article (Downie, Harrison, Raper & Hepworth, 1972) the structure of 2-thioamidopyridine was described and the results compared with the previously reported data for 4-thioamidopyridine (Colleter & Gadret, 1967). The structure of the 2-propyl derivative of 4-thioamidopyridine has also been re-

ported (Colleter, Gadret & Gourselle, 1970). The structural interest in these compounds has centred on the parameters of the thioamide group and the consequent electron arrangement within the group. Additional features of interest have been the non-coplanarity of the pyridine ring with the thioamide group and the hydrogen-bonding schemes. These features of interest are reviewed in this article.

In addition to these items of structural interest the thioamidopyridines have wide-ranging chemical, biochemical and industrial applications. The anti-tuber-

cular activity of 4-thioamidopyridine and its derivatives have been the major reason for the structural investigation of those compounds by Colleter and his group. Sutton (1963, 1966) has described the chelating ability of 2-thioamidopyridine and 6-propyl-2-thioamidopyridine (Sutton, 1971) towards metals. In addition to its chelating ability, 2-thioamidopyridine is a useful inhibitor of the corrosion of carbon steels in dilute sulphuric acid (Downie *et al.* 1972). The commercial applications of 3-thioamidopyridine include its use as a levelling agent in 'bright zinc electroplating'. The compound has three possible coordination sites and forms a neutral complex with zinc iodide (McNeill, 1972). The infrared spectrum of this complex strongly suggests the compound to be N-bonded to zinc. The coordinating ability of 3-thioamidopyridine towards zinc and the use of the compound as a 'leveller' in zinc electroplating are believed to be not unrelated. Consequently this structural investigation has been undertaken as part of a continuing programme of work involving examination of the factors associated with corrosion inhibition and related phenomena.

Experimental

Crystal data

The compound was obtained from Ralph Emmanuel Ltd. Yellow needle-shaped crystals, elongated in the

[001] direction, were obtained on evaporation from ethanolic solution.

Unit-cell parameters were obtained initially from Weissenberg ($\lambda\text{Cu } K\alpha = 1.5418 \text{ \AA}$) and precession ($\lambda\text{Mo } K\alpha = 0.7107 \text{ \AA}$) photographs of the $hk0$, $k0l$ and $0kl$ nets. On the basis of systematic absences deduced from these and higher layer Weissenberg photographs, the compound was allocated to space group $P2_1/c$. However, the initial orientation of the crystal on the Hilger-Watts four-circle automatic diffractometer in this space group proved difficult because no strong reflexions of type $h00$ were available. This is a common feature of thioamidopyridines and is a consequence of the molecular packing. The crystal was consequently aligned in space group $P2_1/n$ and this space-group symmetry was used in the structure determination. The positions of twelve reflexions, with respect to the four circles, were fixed by means of an automatic peak-finder program. The orientation matrix was defined and the unit-cell dimensions were refined from the coordinates of these reflexions. The crystal density was determined by flotation in a mixture of 1-bromopropane and bromobenzene.

Table 1 contains the crystal and experimental data for the compound.

Data collection and reduction

A crystal of dimensions $0.28 \times 0.18 \times 0.13 \text{ mm}$ together with Mo $K\alpha$ radiation and a 3.5 mm collimator was used to collect the data. A θ - 2θ scan was employed in the data collection out to $2\theta = 50^\circ$. Each scan consisted of 60 steps at 0.01° intervals with a counting time of 3 sec per step; two stationary background counts of 30 sec were recorded at either end of the scan. As a check against electronic and crystal stability during the process of data collection, the intensities and coordinates of three standard reflexions (002, 103 and 041) were checked after every 50 reflexions. No significant deviations were detected. Intensities were recorded for reflexions of type hkl , $\bar{h}kl$ and their symmetry-related equivalents, $h\bar{k}l$ and $hk\bar{l}$. The intensities of the equivalent reflexions were averaged prior to correction for Lorentz and polarization effects, giving a final data set consisting of reflexions of type hkl and $h\bar{k}l$. Only observed data were included in the final set. The intensity

Table 1. Crystal and experimental data

Formula	$\text{C}_6\text{H}_6\text{N}_2\text{S}$
M.W.	138.20
Unit cell	
a	4.004 (2) \AA
b	10.572 (5)
c	15.400 (7)
β	96.42 (4) $^\circ$
V	647.80 \AA^3
ρ calculated	1.42 g cm^{-3}
ρ determined	1.41
Systematic absences	$h0l: h+l=2n+1$ $h00: h=2n+1$ $0k0: k=2n+1$ $00l: l=2n+1$
Space group	$P2_1/n$
Z	4
$\mu\text{Mo } K\alpha$	3.88 cm^{-1}
$F(000)$	288

Table 2. Atomic and thermal parameters. The values of b_{ij} are defined by the expression $\exp[-\frac{1}{4}(h^2a^2b_{11} + 2hka^*b^*b_{12} + \dots)]$

	Non-hydrogen atoms parameters $\times 10^5$.								
	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
S(7)	14437	17586	7613	6860	533	311	33	-315	862
N(1)	78503	21522	32785	7006	638	322	-226	-234	-242
N(7)	33759	-5912	10361	8821	498	350	-160	-1327	996
C(2)	63638	19030	24781	6233	483	295	-72	45	53
C(3)	48318	7586	22497	4824	451	252	-40	-10	231
C(4)	48153	-1547	28828	6007	527	293	-106	342	-1
C(5)	62606	1027	37160	7911	733	294	149	11	398
C(6)	77882	12607	38813	8483	727	275	-43	-296	-208
C(7)	32528	5608	13386	4325	527	298	-29	181	45

Table 2 (cont.)

Hydrogen atoms parameters $\times 10^3$			$B(\text{\AA}^2 \times 10^3)$		
H(2)	4503	25473	20215	2928	
H(4)	35162	-9271	28140	4538	
H(5)	65918	-5646	40995	4442	
H(6)	92263	15530	44920	5128	
H(7)	44235	-11766	13171	4384	
H(8)	21551	-7651	5745	4566	

limit for observed reflexions was set equal to or greater than 2σ , where σ was expressed in the form:

$$\sigma = \sqrt{(\bar{p}^2 + K\bar{B}_1^2)/N}$$

where \bar{p} is the average of the N peak counts, \bar{B}_1 is the average of the scaled background measurements, and K is the ratio of the time taken to measure the peak to the time taken to measure the background count.

Of the 1148 independent reflexions, 712 were considered to be observed.

Structure determination and refinement

The coordinates of the sulphur atom were obtained from an analysis of the Harker line and sections of a sharpened three-dimensional Patterson function. A

structure-factor calculation based on these coordinates gave an R ($= \sum ||kF_o| - |F_c|| / \sum |kF_o|$) value of 0.54. A Fourier map using the phases based on the sulphur atom coordinates resulted in the location of the nine non-hydrogen atoms. Five cycles of least-squares block-diagonal isotropic refinement reduced R to 0.106, which was further reduced to 0.053 after three cycles of anisotropic refinement. At this stage a difference synthesis revealed the positions of the six hydrogen atoms with peak heights ranging from 0.4 to 0.5 $e\text{\AA}^{-3}$. All the planes were used in the calculation of the difference synthesis. Four further cycles of refinement with isotropic temperature factors for the hydrogen atoms reduced the R value to 0.035. The refinement was completed by two cycles of full-matrix calculations with no further reduction in the R value. No indicated shift in any parameter was greater than one-third of the corresponding standard deviation. A weighting analysis indicated that $\sum W\Delta^2/n$ was independent of F_o and $\sin \theta/\lambda$. The weighting scheme used in the later stages of refinement was:

$$|W = 1/[P_1 + |F_o| + P_2|F_o|^2 + P_3|F_o|^3]^{1/2}$$

with

$$P_1 = 5.26, P_2 = 0.018 \text{ and } P_3 = 1 \times 10^{-4}.$$

Table 3. Observed and calculated structure factors

H K L F _o F _c					H K L F _o F _c					H K L F _o F _c					H K L F _o F _c					H K L F _o F _c					H K L F _o F _c														
0	0	2	33.7	-35.1	0	4	14	11.3	11.7	1	2	-7	11.6	-10.2	1	5	4	10.0	-10.2	1	10	2	13.7	13.9	2	3	7	14.5	-14.0	2	8	0	7.4	6.9	3	4	-4	8.0	7.8
0	0	4	51.1	-53.8	0	7	2	24.5	-24.3	1	2	-9	6.1	6.2	1	8	9	16.2	-15.8	1	8	9	16.2	-15.8	2	7	8	7.9	7.4	3	7	8	7.9	7.4	3	7	8	7.9	7.4
0	0	6	69.6	-40.4	0	7	2	24.5	-24.3	1	2	-4	10.2	-10.3	1	10	8	12.6	-12.3	2	3	9	20.6	-20.4	2	3	9	20.6	-20.4	2	3	9	20.6	-20.4	3	4	-2	11.7	12.2
0	0	8	5.8	4.8	0	7	3	12.1	11.6	1	2	-2	36.7	-36.6	1	7	7	21.6	-20.8	2	10	9	8.9	9.0	2	10	9	8.9	9.0	2	10	9	8.9	9.0	2	10	9	8.9	9.0
0	0	10	4.7	4.9	0	7	4	19.0	-18.3	1	2	-2	9.6	-10.0	1	5	8	11.9	-11.2	2	11	-11	6.2	-6.4	2	11	-11	6.2	-6.4	2	11	-11	6.2	-6.4	3	4	3	4.9	4.5
0	0	12	7.8	8.5	0	7	5	9.1	9.0	1	2	-1	15.5	16.0	2	5	10	11.8	16.1	2	5	10	11.8	16.1	1	11	-2	11.8	11.6	2	8	7	5.7	5.8	3	4	4	21.2	-21.5
0	0	14	4.6	10.0	0	7	6	6.3	-4.2	1	2	0	8.5	8.9	1	5	12	14.5	14.2	1	5	12	14.5	14.2	1	11	5	8.1	7.6	2	5	15	6.6	-6.3	3	4	5.6	5.6	
0	0	16	4.9	6.4	0	7	8	12.1	12.1	1	2	1	34.8	-34.3	1	6	-15	8.5	11.9	1	6	-15	8.5	11.9	2	4	-11	8.0	8.5	2	8	-10	11.5	-11.0	3	4	7	15.5	-13.2
0	0	18	2.5	25.2	0	7	9	22.1	-23.3	1	2	2	30.3	-31.4	1	6	-14	7.6	-7.0	1	6	-14	7.6	-7.0	1	11	4	16.3	-16.6	2	4	-11	15.3	16.1	3	4	6.9	-6.8	
0	0	20	7.4	7.8	0	7	10	14.2	13.6	1	2	3	11.0	10.9	1	6	13	9.0	9.3	1	6	13	9.0	9.3	2	0	-12	17.0	-17.3	2	9	-9	6.0	1.7	3	4	0	11.2	11.0
0	0	22	12.1	11.9	0	7	11	12.7	13.0	1	2	4	30.2	-29.6	1	6	-12	6.4	7.8	1	6	-12	6.4	7.8	1	12	-4	7.0	7.2	2	9	-6	9.1	-9.2	3	5	9	7.4	-7.1
0	0	24	39.6	-34.8	0	7	12	7.5	-7.8	1	2	5	35.3	34.5	1	6	-11	13.1	-13.5	1	6	-11	13.1	-13.5	1	12	-1	11.0	12.3	2	4	-9	12.6	-12.5	3	5	9	13.2	-12.6
0	0	26	25.9	-25.9	0	7	13	19.0	-18.3	1	2	6	15.1	-15.2	1	6	-10	9.5	-9.5	2	9	-9	33.9	33.8	2	9	-9	33.9	33.8	2	9	-9	33.9	33.8	3	5	9	12.7	-12.6
0	0	28	6.2	23.9	0	7	14	5.1	5.1	1	2	7	5.2	5.3	1	6	-9	13.7	-12.7	1	6	-9	13.7	-12.7	2	0	-14	15.0	15.0	2	4	-7	13.0	-14.3	3	5	0	6.6	7.1
0	0	30	14.8	15.2	0	7	15	9.3	9.1	1	2	8	16.2	16.1	1	6	-8	16.2	16.1	2	0	-12	17.0	-17.3	2	0	-12	17.0	-17.3	2	9	5	6.1	5.6	3	5	0	11.8	11.6
0	0	32	23.4	-23.4	0	7	16	20.8	-21.2	1	2	9	7.8	-7.3	1	6	-8	8.3	7.5	2	0	-10	23.2	-23.5	2	4	-3	3.5	-2.7	2	9	5	6.1	5.6	3	5	0	8.0	-6.2
0	0	34	11.5	12.1	0	7	17	5.1	-5.0	1	2	10	21.2	21.8	1	6	-4	21.2	21.8	2	0	-8	12.1	-11.7	2	0	-8	12.1	-11.7	2	9	6	8.1	-8.6	3	5	2	11.0	-10.5
0	0	36	31.8	-31.8	0	7	18	10.7	-10.3	1	2	11	10.7	-10.3	1	6	-4	10.7	-10.3	2	0	-6	13.2	-12.6	2	0	-6	13.2	-12.6	2	9	13.2	-12.6	3	5	3	6.8	-7.8	
0	0	38	20.5	20.6	0	7	19	6.2	6.2	1	2	12	8.8	-8.1	1	6	-1	20.8	21.0	2	0	-4	4.0	4.7	2	0	-4	4.0	4.7	2	10	-6	6.7	-6.5	3	5	6	6.7	-6.5
0	0	40	13.3	-13.0	0	7	20	9.4	9.1	1	2	13	25.1	-25.1	1	6	-2	25.6	25.1	2	0	-2	10.5	-10.9	2	0	-2	10.5	-10.9	2	10	7	7.7	-7.2	3	5	-4	7.4	-7.1
0	0	42	6.3	-5.9	0	7	21	4.7	4.8	1	2	14	15.4	-15.0	1	6	2	15.8	-15.0	2	0	0	18.5	-17.9	2	0	0	18.5	-17.9	2	4	2	13.3	13.3	3	6	-11	11.6	-11.0
0	0	44	16.3	-16.9	0	7	22	11.5	9.5	1	2	15	8.9	8.7	1	6	3	23.5	-23.1	2	0	2	20.8	-21.0	2	4	3	5.8	-5.6	2	10	1	10.6	10.9	3	6	-12	12.7	12.4
0	0	46	5.5	-5.9	0	7	23	15.0	15.3	1	2	16	6.4	-6.2	1	6	4	9.1	-8.8	2	0	4	12.0	11.6	2	4	4	9.5	9.5	2	10	2	7.1	-5.9	3	6	-6	7.7	-7.8
0	0	48	15.0	1.8	0	7	24	10.7	-10.4	1	2	17	5.8	5.1	1	6	5	18.7	-18.3	2	0	6	15.5	-15.0	2	4	5	15.1	-15.0	2	10	5	11.0	-10.7	3	6	-5	17.7	17.8
0	0	50	34.3	-34.4	0	7	25	14.0	10.1	1	2	18	6.7	-6.8	1	6	6	12.7	12.9	2	0	8	10.5	-10.5	2	4	6	12.8	-12.6	2	10	5	10.5	-11.7	3	6	-4	7.1	-6.8
0	0	52	2.6	2.5	0	7	26	4.0	4.0	1	2	19	14.8	-14.5	1	6	7	18.8	-18.5	2	0	10	17.1	-17.0	2	4	7	18.8	-18.5	2	10	3	6.8	11.1	3	6	-3	6.0	5.5
0	0	54	26.4	-25.5	0	7	27	10.7	10.8	1	2	20	7.3	7.4	1	6	9	25.8	25.9	2	0	12	17.9	-17.9	2	4	10	5.3	5.0	2	11	-2	7.1	7.3	3	6	-1	12.1	-12.7
0	0	56	37.3	-35.0	0	7	28	15.3	15.3	1	2	21	11.5	11.3	1	6	10	14.5	-14.5	2	0	14	19.2	-19.2	2	4	11	11.5	11.3	2	11	-1	7.6	7.6	3	6	3	12.7	-12.5
0	0	58	21.5	-21.6	0	7	29	11.3	11.3	1	2	22	11.5	15.7	1	6	13	7.4	8.4	2	0	16	21.5	21.4	2	4	13	7.4	8.4	2	11	1	12.7	-13.6	3	6	2	5.2	5.0
0	0	60	4.9	3.5	0	7	30	7.5	-8.6	1	2	23	14.7	15.0	1	6	14	8.6	-8.3	2	0	18	14.7	15.0	2	4	14	8.6	-8.3	2	11	3	10.9	-9.6	3	6	5.6	-6.4	
0	0	62	7	14.9	14.4	0	10	8	13.2	13.0	1	2	24	11.3	-11.0	1	7	9	13.4	-13.3	2	0	19	13.4	-13.3	2	4	15	11.3	-11.2	2	11	3	12.2	-12.4	3	6	5.8	5.2
0	0	64	32.5	32.0	0	10	8	7.7	-7.6	1	2	25	23.0	22.7	1	7	9	8.6	-8.4	2	0	20	11.0	-10.8	2	4	16	8.3	-8.0	2	11	5	10.6	10.4	3	6	5.1	11.7	11.0
0	0	66	5.3	5.5	0	10	9	11.7	-11.7	1	2	26	11.7	-11.7	1	7	10	11.6	11.5	2	0	21	11.0	-10.8	2	4	17	11.0	-10.8	2	11	5	9.9	-9.2	3	6	5.2	10.7	10.7
0	0	68	10.7	10.6	0	10	9	19.9	20.3	1	2	27	11.7	-11.7	1	7	10	11.6	11.5	2	0	22	11.0	-10.8	2	4	18	11.0	-10.8	2	11	5	10.2	-10.4	3	6	-10	5.8	-5.5
0	0	70	11.7	10.6	0	10	9	8.4	-8.6	1	2	28	6.5	6.5	1	7	10	15.6	15.9	2	0	23	11.0	-10.8	2	4	19	11.0	-10.8	2	11	5	10.1	-10.1	3	6	-10	10.3	-10.6
0	0	72	30.2	-30.8	0	10	11	13.5	-13.5	1	2	29	9.2	-9.2	1	7	11	9.2	-9.1	2	0	24	11.0	-10.8	2	4	20	11.0	-10.8	2	11	5	14.0	14.0	3	6	-10	10.5	-10.0
0	0	74	5.0	-5.6	0	11	1	9.8	9.4	1	2	30	3.7	3.7																									

Atomic scattering factors for S, N and C were taken from *International Tables for X-ray Crystallography* (1962). The scattering curve for H was that of Stewart, Davidson & Simpson (1965).

The final atomic and thermal parameters are listed in Table 2; observed and calculated structure factors are in Table 3.

Table 4. Bond lengths and angles with e.s.d.'s in parentheses

(a) Bond lengths	
S(7)–C(7)	1.666 (4) Å
N(1)–C(2)	1.334 (5)
N(1)–C(6)	1.325 (5)
N(7)–C(7)	1.307 (5)
N(7)–H(7)	0.84 (5)
N(7)–H(8)	0.84 (5)
C(2)–C(3)	1.384 (5)
C(2)–H(2)	0.98 (4)
C(3)–C(4)	1.373 (5)
C(3)–C(7)	1.488 (5)
C(4)–C(5)	1.375 (6)
C(4)–H(4)	0.97 (5)
C(5)–C(6)	1.379 (6)
C(5)–H(5)	0.92 (5)
C(6)–H(6)	1.09 (5)
(b) Bond angles	
C(2)–N(1)–C(6)	117.8 (3)
C(7)–N(7)–H(7)	123 (3)
C(7)–N(7)–H(8)	118 (3)
H(7)–N(7)–H(8)	119 (5)
N(1)–C(2)–C(3)	123.2 (3)
N(1)–C(2)–H(2)	118 (2)
C(3)–C(2)–H(2)	118 (2)
C(2)–C(3)–C(4)	118.1 (3)
C(2)–C(3)–C(7)	119.5 (3)
C(4)–C(3)–C(7)	122.4 (3)
C(3)–C(4)–C(5)	119.3 (4)
C(3)–C(4)–H(4)	124 (3)
C(5)–C(4)–H(4)	116 (3)
C(4)–C(5)–C(6)	118.7 (4)
C(4)–C(5)–H(5)	118 (3)
C(6)–C(5)–H(5)	122 (3)
N(1)–C(6)–C(5)	123.0 (4)
N(1)–C(6)–H(6)	111 (2)
C(5)–C(6)–H(6)	126 (2)
S(7)–C(7)–N(7)	123.4 (3)
S(7)–C(7)–C(3)	120.7 (3)
N(7)–C(7)–C(3)	116.0 (3)

Description and discussion of the structure

Bond lengths, bond angles and their e.s.d.'s are listed in Table 4.

Planarity in the molecule

The details of some planes of best fit are given in Table 5. The χ^2 test was used to determine planarity and, as expected, the pyridine ring is planar within experimental error. The S(7) and N(7) atoms of the side-chain are considerably displaced from the plane of the pyridine ring, but the C(7) atom of the thioamido group is not significantly displaced from this mean plane.

Table 5. Equations of some mean planes and displacements of atoms from these planes

Each mean plane is represented by an equation of the type $lX + mY + nZ - P = 0$ referred to an orthogonal system of axes, which has X along the a axis, Y in the a, b plane and Z along the c^* axis.

(a) Pyridine ring

$$0.8986X - 0.3630Y - 0.2464Z - 0.2501 = 0$$

Displacements and e.s.d.'s (Å)

$$S(7) - 0.810 (1)$$

$$N(7) + 0.641 (4)$$

$$C(7) - 0.007 (4)$$

Pyridine ring atoms average 0.008 Å displacement.

(b) Thioamido side chain + C(3)

$$0.9149X + 0.2090Y - 0.3453Z - 0.3952 = 0$$

Displacements and e.s.d.'s (Å)

$$S(7) \quad 0.000 (1) \quad C(3) - 0.001 (1)$$

$$N(7) \quad 0.000 (4) \quad H(7) \quad 0.062 (47)$$

$$C(7) \quad 0.002 (4) \quad H(8) - 0.169 (47)$$

The plane formed by the five atoms of the side chain (*i.e.* including the two hydrogen atoms) and the C(3) atom in the pyridine ring has also been calculated. Again the χ^2 value was satisfactory and indicated a planar arrangement of the atoms.

The mean plane through the pyridine ring and the mean plane through the thioamide group are inclined at an angle of 33.8° to one another. This non-coplanarity

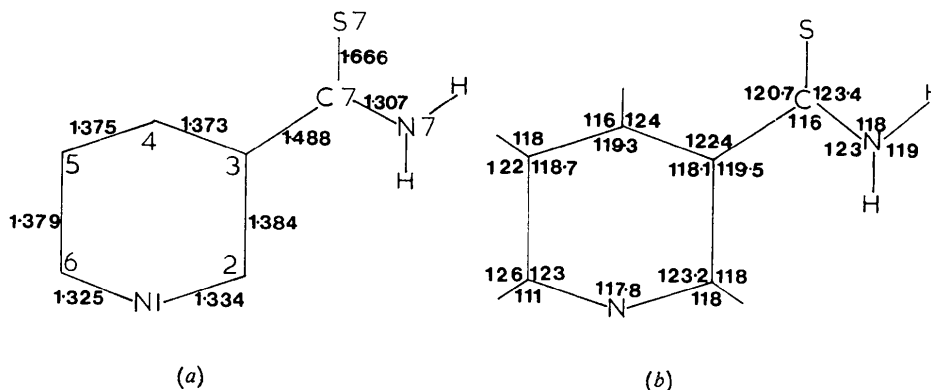


Fig. 1. (a) Bond lengths and (b) bond angles in 3-thioamidopyridine.

Table 6. *Dihedral angles*

Compound	Angle between planes	Reference
2-Thioamidopyridine	10.5°	Downie <i>et al.</i> (1972)
3-Thioamidopyridine	33.8	This work
4-Thioamidopyridine	38	Colleter & Gadret (1967)
2-Propyl-4-Thioamidopyridine	34	Colleter <i>et al.</i> (1970)

is not uncommon and Takano, Sasada & Kakudo (1966) have suggested that it arises because of steric hindrance between the atoms in the side chain and the ring atoms *ortho* to the side chain. Takano *et al.* (1966) calculated non-bonded contacts for the relevant atoms in a number of related compounds, and showed that for a given pair of atoms the distance was reasonably constant, and close to the expected van der Waals distances for these atoms. The angular displacements for the three isomers of thioamidopyridine and for 2-propyl-4-thioamidopyridine are listed in Table 6. In 3-thioamidopyridine, the *ortho* non-bonded contacts are between S(7) and H(2) and N(7) and C(4). The respective distances are 2.76 and 2.88 Å, which are significantly shorter than the sum of the van der Waals radii (S = 1.85 Å and N = 1.50 Å, Pauling, 1960). However, Pauling (1960) has concluded that the non-bonded radius of an atom in directions close to the bond direction (*i.e.* within 35°) is about 0.5 Å less than the van der Waals radius. The corresponding *ortho* contacts for the thioamidopyridines and 2-propyl-4-thioamidopyridine are given in Table 7.

Table 7. *Non-bonded ortho intramolecular contacts*

Compound	Contact	Length (Å)
2-Thioamidopyridine	S...CH	3.15
	N...NH	2.62
3-Thioamidopyridine	S...HC	2.76
	N...CH	2.88
4-Thioamidopyridine	S...CH	2.96
	N...NH	2.75
2-Propyl-4-thioamidopyridine	S...HC	2.63

Pyridine ring dimensions

Fig. 1(a) and (b) respectively illustrate bond lengths and angles in the molecule.

In 3-thioamidopyridine the pyridine ring has C-C distances of 1.378 Å with a r.m.s. deviation of 0.005 Å and C-N distances of 1.330 Å with a r.m.s. deviation of 0.006 Å. Similar data for all the thioamidopyridines are listed in Table 8. The pyridine ring dimensions among the thioamido derivatives exhibit no significant differences from each other and are all similar to the data for the free pyridine molecule obtained by Bak, Hansen & Rastrup-Andersen (1954). Consequently the pyridine ring appears to be largely unaffected as a result of substitution by a thioamide group.

Thioamido side-chain dimensions

Bond lengths and angles in the side chain of the molecule are illustrated in Fig. 1(a) and (b). Table 9

lists the side-chain dimensions from the isomeric thioamidopyridines and 2-propyl-4-thioamidopyridine.

Table 8. *Average pyridine ring dimensions for a number of thioamidopyridine systems*

The r.m.s. deviations are given in parentheses.

Compound	C-C (Å)	C-N (Å)
2-Thioamidopyridine	1.383 (6)	1.336 (3)
3-Thioamidopyridine	1.378 (5)	1.330 (6)
4-Thioamidopyridine	1.41 (1)	1.34 (3)
2-Propyl-4-thioamidopyridine	1.40 (1)	1.355 (7)

Table 9. *Side-chain dimensions (Å) in thioamidopyridine*

Compound	C-C	C-N	C-S
2-Thioamidopyridine (Downie <i>et al.</i> , 1972)	1.505	1.325	1.657
3-Thioamidopyridine (This work)	1.488	1.307	1.666
4-Thioamidopyridine (Colleter <i>et al.</i> , 1967)	1.49	1.32	1.65
2-Propyl-4-thioamidopyridine (Colleter <i>et al.</i> , 1970)	1.51	1.33	1.67

The planarity in the side-chain and the angles around C(7) indicate sp^2 hybridization in that atom. The C(3)-C(7) bond length (1.488 Å), which connects the pyridine molecule to the side chain, is significantly longer than 1.466 Å (Brown 1964) which is expected for a $C[sp^2]-C[sp^2]$ bond. Kuchitsu, Fukuyama & Morino (1968) have demonstrated that the attachment of oxygen atoms onto the carbon atoms of a pure $C[sp^2]-C[sp^2]$ bond lengthens such a bond. The influence of the sulphur and nitrogen atoms in the thioamide side chain produces a similar effect in the C(3)-C(7) bond in this structure and on the related bond in the other thioamidopyridines. Beagley, Brown & Monaghan (1969) have considered the possible interpretations of unusually long $C[sp^2]-C[sp^2]$ bonds and have concluded that

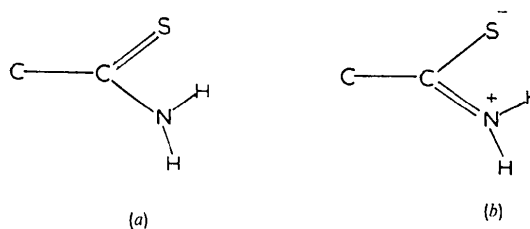


Fig. 2. Canonical forms of the thioamido group: (a) amide form, (b) ionic form.

variations in hybridization states have limited effect and that the principle factors are conjugation and hyperconjugation. Consequently the long $C[sp^2]-C[sp^2]$ bonds in the thioamidopyridines, which do not differ significantly from one another, are interpreted in terms of conjugation between the side chain and the pyridine molecule.

The C(7)–S(7) (1.666 Å) and the C(7)–N(7) (1.307 Å) bond lengths of 3-thioamidopyridine show the same significant shortening from accepted single-bond values which are exhibited by its isomers and by 2-propyl-4-thioamidopyridine (Table 9). Abrahams's (1956) carbon–sulphur order/length curve gives 79% double-bond character for the C(7)–S(7) bond and Wheatley's (1955) carbon–nitrogen order/length curve gives 53% double-bond character for the C(7)–N(7) bond. There are minor variations in the C–S distances (Table 9) among the thioamidopyridines and one significant difference among the C–N bond lengths. The C–N distance in 3-thioamidopyridine is significantly shorter than the corresponding value for 2-thioamidopyridine. The C–S distance is also slightly longer in this structure and points to a slightly modified electron distribution relative to 2-thioamidopyridine. In valence-bond terms this would be explained in terms of a slightly greater contribution of the ionic canonical form (Fig. 2) in the overall resonance structure of 3-thioamidopyridine.

The reductions in length of the C(7)–S(7) and the C(7)–N(7) bonds in this structure compared with the corresponding values (1.713 and 1.325 Å respectively) in thioacetamide (Truter, 1960) support the previous interpretations of the C(3)–C(7) bond length. That is, conjugation between the thioamido side chain and the

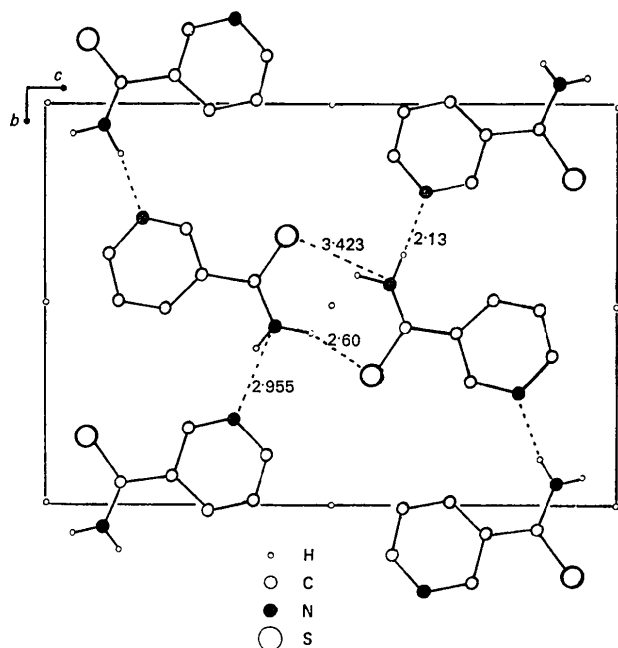


Fig. 3. 3-Thioamidopyridine, molecular packing and hydrogen bonding in a^* projection.

pyridine ring and a subsequent withdrawal of electron density from the C(3)–C(7) bond into the side-chain.

In 3-thioamidopyridine and the related structures the indications are that all three atoms in the side chain are involved in multiple bonding. Further evidence for the involvement of an ionic as well as a conventional amide canonical form (Fig. 2) comes from the fact that the angles around N(7) are 120° , within experimental error, and the hydrogen atoms attached to N(7) are coplanar with the other atoms in the side chain. The delocalization of the four π electrons of the side chain may also be explained in terms of the formation of molecular orbitals from the p_z orbitals of C(7) and N(7) and presumably S(7), although d -orbital participation cannot be excluded in the latter atom.

Molecular packing and hydrogen-bonding

The molecular packing and hydrogen-bonding schemes are illustrated in Fig. 3, which is an a^* projection. Table 10 contains the shortest (less than 4.0 Å) non-bonding contacts and Table 11 lists some N–H...S distances.

Table 10. Shortest non-bonding intermolecular contacts

Equivalent position	Symmetry code		
x, y, z			1
$\bar{x}, \bar{y}, \bar{z}$			–1
$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$			2
$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$			–2
	Symmetry code	Cell	Length
†S(7)···N(7)	–1	101	3.423 (4) Å
S(7)···C(2)	1	100	3.515 (4)
S(7)···C(6)	2	001	3.661 (4)
S(7)···H(2)	1	100	3.05 (3)
S(7)···H(6)	2	001	2.96 (5)
†S(7)···H(8)	–1	101	2.60 (5)
*N(1)···H(7)	–2	100	2.955 (5)
N(1)···C(4)	–2	000	3.543 (5)
N(1)···H(4)	–2	000	3.10 (4)
*N(1)···H(7)	–2	100	2.13 (4)
N(7)···N(7)	–1	011	3.790 (6)
N(7)···C(6)	–2	000	3.662 (6)
C(2)···C(4)	–2	100	3.538 (5)
C(2)···H(4)	–2	100	3.14 (4)
C(4)···H(2)	–2	000	2.85 (4)
C(6)···H(8)	–2	100	2.96 (5)
H(2)···H(4)	–2	100	2.57 (6)
H(5)···H(6)	–1	100	2.79 (7)
H(6)···H(7)	–2	000	2.79 (7)
H(8)···H(8)	–1	111	2.84 (7)

* Hydrogen bond N(1)···H(7)–N(7).

† Hydrogen bond S(7)···H(8)–N(7).

The packing diagram is similar to the other thioamidopyridines in which the molecules lie mainly in the b, c plane and are stacked in the direction of the a axis. For all these molecules the a axis is just slightly greater than 3.5 Å. Location of the hydrogen atoms revealed two separate types of hydrogen bond. Contacts of type N–H...S (3.423 Å) connect pairs of molecules across symmetry centres, while contacts of type N–H...N (2.955 Å) connect molecules *via* a screw axis. These

Table 11. *Intermolecular N-S distances*

N-H...S Distance (Å)	Molecule	Reference
3.396 } 3.420 } 3.469 } 3.504 }	Thioacetamide	Truter (1960)
3.44	4-Thioamidopyridine	Colleter & Gadret (1967)
3.449 } 3.499 }	1-Thiocarbamoyl- imidazolidine-2-thione	Valle, Cojazzi, Busetti & Mammi (1970)
3.39	Propyl-2-thiocarbamoyl- -4-pyridine	Colleter <i>et al.</i> , (1970)
3.43	2-Thioamidopyridine	Downie <i>et al.</i> , (1972)
3.423	3-Thioamidopyridine	This work

hydrogen bonds are two-dimensional in character being restricted to the *b, c* plane; the contacts in the direction of the *a* axis are of the van der Waals type.

The N(7)–H...S(7) bond is slightly longer than the sum of the van der Waals radii (N = 1.50 and S = 1.85 Å). However, the contact is within the range expected for similar bonds (Downie *et al.*, 1972) and variations in the van der Waals radii of sulphur are common. This hydrogen bond is linear, within experimental error, and the S...H contact of 2.60 Å indicates a significant interaction between these atoms.

Hydrogen bonds of the type N–H...N, which involve the thioamide nitrogen as the donor and the pyridine nitrogen as the acceptor atom, are a feature of the intermolecular contacts formed by all the thioamidopyridines, with the exception of 2-thioamidopyridine where the proximity of the pyridine nitrogen and the thioamide nitrogen prevents such a contact from being formed.

The N(1)...N(7) distance in 3-thioamidopyridine is 2.955 Å, slightly less than the sum of the van der Waals radii. The values in the other structures are 4-thioamidopyridine, 2.90 Å and 2-propyl-4-thioamidopyridine 2.91 Å. The bond is linear, within experimental error, and there is a significant shortening of the contact between the pyridine nitrogen and the amide hydrogen of the side chain [N(1)–H(7) = 2.13 Å].

Summary

The results of the structure analysis of 3-thioamidopyridine show that the pyridine ring dimensions are scarcely affected as a result of substitution by a thioamide group. The differences in the bond lengths of the thioamide group in 3-thioamidopyridine compared with 2-thioamidopyridine are attributed to a larger contribution from the ionic-canonical form in the case of 3-thioamidopyridine. All the thioamidopyridines show extensive H-bonding in the solid, forming both N–H...N and N–H...S bonds; 2-thioamidopyridine only forms N–H...S bonds because of the proximity of the pyridine nitrogen and the side-chain. All the compounds pack in the solid state in a similar manner, consisting of H-bonded dimers in the *b, c* plane stacked in the direction of the *a* axis, where the contacts are of the normal van der Waals type.

All the calculations were performed on the IBM 360/67 computer in the Computing Centre at the University of Newcastle upon Tyne. The programs used throughout the analysis, in addition to small local programs, were from the integrated set derived for the IBM 360 by Dr F. R. Ahmed and his group at N.R.C., Ottawa, Canada. The *SFLS* block-diagonal refinement program was modified for full-matrix refinement by Dr H. M. M. Shearer of Durham University.

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References

- ABRAHAMS, S. C. (1956). *Quart. Rev.* **10**, 407–436.
 BAK, B., HANSEN, L. & RASTRUP-ANDERSEN, J. (1954). *J. Chem. Phys.* **22**, 2013–2017.
 BEAGLEY, B., BROWN, D. P. & MONAGHAN, J. J. (1969). *J. Mol. Struct.* **4**, 233–244.
 BROWN, M. G. (1959). *Trans. Faraday. Soc.* **55**, 694–701.
 COLLETER, J. C. & GADRET, M. (1967). *Bull. Soc. Chim. France*, pp. 3463–3469.
 COLLETER, J. C., GADRET, M. & GOURSELLE, M. (1970). *Acta Cryst.* **B26**, 1510–1518.
 DOWNIE, T. C., HARRISON, W., RAPER, E. S. & HEPWORTH, M. A. (1972). *Acta Cryst.* **B28**, 283–290.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 KUCHITSU, K., FUKUYAMA, T. & MORINO, Y. (1968). *J. Mol. Struct.* **1**, 463–479.
 MCNEILL, W. S. (1972). B. Sc. Project Thesis, Department of Chemistry, Newcastle upon Tyne Polytechnic.
 PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 SUTTON, G. J. (1963). *Aust. J. Chem.* **16**, 1137–1140.
 SUTTON, G. J. (1966). *Aust. J. Chem.* **19**, 2059–2068.
 SUTTON, G. J. (1971). *Aust. J. Chem.* **24**, 919–924.
 TAKANO, T., SASADO, Y. & KAKUDO, M. (1966). *Acta Cryst.* **21**, 514–522.
 TRUTER, M. R. (1960). *J. Chem. Soc.* pp. 997–1007.
 VALLE, G., COJAZZI, G., Busetti, V. & MAMMI, M. (1970). *Acta Cryst.* **B26**, 468–477.
 WHEATLEY, P. J. (1955). *Acta Cryst.* **8**, 224–226.