place slowly at room temperature but the kinetics of the process has not been studied as extremely long times are involved.

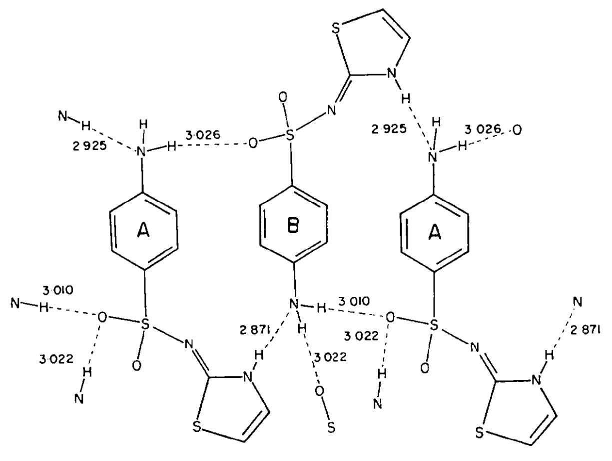

Fig. 5. The hydrogen bonding in sulphathiazole III.

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The Crystal and Molecular Structure of 2-Thioamidopyridine

By T. C. Downie*, W. Harrison† and E. S. Raper‡
Department of Chemistry, Newcastle-upon-Tyne Polytechnic, Newcastle-upon-Tyne, England

and M. A. Hepworth
Magnesium Elektron Ltd, Manchester, England

(*Received* 2 *December* 1970)

Crystals of 2-thiamidopyridine, $C_6H_6N_2S$, are monoclinic, space group $P2_1/c$ with four molecules in a unit cell of dimensions $a=5{\cdot}79$, $b=7{\cdot}42$ and $c=16{\cdot}26$ Å, $\beta=106{\cdot}9°$. The crystal structure was solved by three-dimensional Patterson and Fourier syntheses using the heavy-atom technique. The atomic parameters were refined by block-matrix least-squares calculations. Hydrogen atoms were located but their parameters were not refined. The final R index was 0·069 from 1004 observed reflexions, collected using Cu $K\alpha$ radiation. The mean bond lengths are C–C = 1·383, C–N = 1·336 Å in the pyridine ring and C–C = 1·505, C–N = 1·325, C–S = 1·657 Å in the thioamido group with a mean e.s.d. of 0·006 Å. Bond lengths and angles in the thioamido group suggest that the electron configuration contains contributions from the ionic canonical form as well as the amide form. The angle between the plane of the pyridine ring and that of the thioamido group is 10·5°. Non-bonded contact radii of some atoms are proposed to interpret the twisting between the thioamido group and the pyridine ring. Pairs of hydrogen bonds of the type N–H···S and 3·43 Å in length join molecules together across centres of symmetry.

Introduction

The corrosion inhibitive properties of aliphatic and aromatic amines, as well as nitrogen heterocyclic compounds, have been known for some time. (Rhodes & Khun, 1929; Mann, Lauer & Hultin, 1936). Sulphur-containing compounds such as thiourea derivatives and mercapto-imidazole derivatives have also been extensively used as inhibitors. (Aronson & Belen'kii, 1964). In view of the chelating ability of 2-thioamidopyridine (2-thiopic) to group IIB metals (Sutton, 1963) and certain transition metals (Sutton, 1966) the corrosion inhibitive properties of 2-thiopic were investigated, the compound was found to reduce the corrosion rate of carbon steels in 0·2N sulphuric acid by 40%. (Osborne, 1968).

In its chelation with metals, 2-thiopic always uses its pyridine nitrogen atom as well as either the nitrogen atom or the sulphur atom of the side chain. Spectro-

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* Present address: Thames Polytechnic, Wellington St., Woolwich, London S.E.18, England.

† Present address: University of British Columbia, Vancouver, Canada.

‡ To whom enquiries should be addressed.

scopic studies have been used on individual complexes to indicate which of the side chain atoms is involved. Accurate dimensions of the thioamido side chain would facilitate an understanding of the electron distribution within the functional group and thereby assist understanding of the formation of the chelates.

A structural investigation of thiopic has consequently been undertaken as part of a programme of work involving examination of the factors associated with corrosion inhibition and also because of its inherent structural and chemical interest.

The crystal structure of the *para* isomer of 2-thiopic, namely 4-thioamido (thiocarbamoyl-4) pyridine, (4-thiopic) has been published previously (Colleter & Gadret, 1967) and a comparison of the two compounds is included.

However, as a result of the displacement of the thioamido side chain from the *ortho* to the *para* position 4-thiopic does not offer the same potential as a chelating agent as does 2-thiopic.

Experimental

Crystal data

The compound was supplied by Dr G. J. Sutton of the University of New South Wales, Australia. Suitable crystals were grown by slow evaporation from alcoholic solution. The substance crystallized in the

Table 1. *Crystal and experimental data for two and four thioamido pyridine* (2-*thiopic and* 4-*thiopic*)

	2-Thiopic		4-Thiopic (Colleter & Gadret, 1967)
Formula	–	$C_6H_6N_2S$	–
Molecular weight	–	138·2	–
Unit cell:			
a	$5{\cdot}79 \pm 0{\cdot}01$ Å		$3{\cdot}836 \pm 0{\cdot}01$ Å
b	$7{\cdot}42 \pm 0{\cdot}03$		$10{\cdot}710 \pm 0{\cdot}01$
c	$16{\cdot}26 \pm 0{\cdot}05$		$16{\cdot}140 \pm 0{\cdot}01$
β	$106{\cdot}9 \pm 0{\cdot}2°$		$96°50' \pm 2'$
V	668·38 $Å^3$		662·06 $Å^3$
Crystal density, $g.cm^{-3}$			
calculated (D_c)	1·40		–
determined (D_m)	1·37		–
Systematic absences	–	hkl: no conditions	–
and	–	$h0l: 1=2n$	–
space group	–	$0k0: k=2n$	–
	$P2_1/c$ (C_{2h}^5)		$P2_1/c$ (C_{2h}^5)
Z (number of molecules in the unit cell)	4		4
linear absorption coefficient μ (Cu $K\alpha$)	–	30·75 cm^{-1}	–
Total number of electrons $F(000)$	–	288	–
Number of observed reflexions	1004		664
Final R index	0·069		0·094

Table 2. *Atomic and thermal parameters*

The values of b_{ij} are defined by the expression $\exp\,[-\frac{1}{4}(h^2a^{*2}b_{11}+2hka^*b^*b_{12}+\ \ldots)]$

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	23333	19354	3138	1750	1928	620	−596	695	−149
N(1)	77446	49321	16572	2837	2063	405	−282	318	−389
N(2)	70752	19108	7843	1997	2018	505	−369	574	358
C(1)	81894	65371	20471	4565	2313	525	−770	705	−1735
C(2)	64412	78233	20125	6258	1907	544	−599	1769	−1426
C(3)	41017	74528	15403	5481	1662	639	45	2059	1036
C(4)	35839	57863	11355	3397	1661	504	41	1009	710
C(5)	54666	45863	12053	2500	1487	304	154	758	412
C(6)	50595	27700	7742	2008	1493	308	84	456	635

Hydrogen atoms parameters $\times 10^3$

				B (isotropic) $Å^2 \times 10^3$
H(1)	991	681	239	4438
H(2)	683	901	231	4866
H(3)	278	837	158	4412
H(4)	187	550	78	3337
H(5)	868	255	104	3161
H(6)	700	074	46	3161

form of yellow needles of uniform cross section, elongated along the [100] direction. The two isomeric compounds seem to be of very similar crystal habit.

Unit-cell parameters (Table 1) were determined from precession photographs of the *hk*0, 0*kl* and *h*0*l* reciprocal lattice nets using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). The crystal density was measured by the flotation method in a mixture of 1-bromopropane and 2-bromobenzene.

Data collection and reduction

Two crystals were used for the intensity data collection. For the *a*-axis photographs ($h = 0 \rightarrow 3$) the crystal had dimensions $0{\cdot}4 \times 0{\cdot}4 \times 0{\cdot}4$ mm and for the *b*-axis photographs ($k = 0 \rightarrow 4$) the crystal was of dimensions $0{\cdot}6 \times 0{\cdot}6 \times 0{\cdot}6$ mm. Nickel filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) was used for the data collection. Integrated intensities were measured using a Joyce–Loebl integrating 'flying spot' microdensitometer.

The reflexions were corrected for Lorentz and polarization effects, but no correction for spot length was made since the microdensitometer accommodates variations in reflexion profiles. The structure amplitudes were placed on a common scale by means of a program based on the method of Monahan, Schiffer & Schiffer (1967). No absorption corrections were applied in view of the small μ value (Table 1) and the fairly small crystal sizes employed. A total of 1004 observed structure amplitudes was recorded.

Table 1 lists the crystal and experimental data for this compound (2-thiopic) and its *para* isomer (4-thiopic).

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 the sulphur atom coordinates gave a value of $R(= \sum ||kF_o| - |F_c|| / \sum |kF_o|) = 0{\cdot}49$. A Fourier synthesis, using the phases based on the sulphur atom coordinates was computed which revealed all the light non-hydrogen atoms. A second structure-factor calculation based on all the atoms, excluding hydrogen, reduced R to 0·23.

At this stage refinement was commenced of the positional and thermal parameters by the method of least squares (block-diagonal approximation). After four cycles of isotropic and five cycles of anisotropic refinement R had fallen to 0·082. The accelerated refinement device devised by Hodgson & Rollett (1963) incorporating a series of 'fudge' factors was employed. A three-dimensional difference Fourier synthesis was then computed. Six peaks ranging in height from 1·0 to 1·6 e.Å^{-3} were observed and found to correspond to the six hydrogen atoms. Two further cycles of refinement were performed with the hydrogen atom contributions to the structure-factor calculations included. The hydrogen atoms were given isotropic temperature factors equal to those of the atoms to which they were attached. For these two cycles a fudge factor of 0·8 was used. The R value at this stage was 0·069 and refinement was terminated since no indicated shift was greater than 0·003 Å for positional parameters and 0·0007 Å^{-2} for thermal parameters. A weighting analysis indicated that $\sum W\Delta^2/n$ was independent of F_o and $\sin\theta/\lambda$. The weighting scheme in the final stages of refinement was

$$\sqrt{W} = [1/1 + ([k|F_o| - b]/a)^2]^{1/2}$$

with $a = 11{\cdot}20$ and $b = 7{\cdot}00$.

Atomic scattering factors were obtained from *International Tables for X-ray Crystallography* (1962).

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

Table 3. *Observed and calculated structure factors*

[illegible]

Description and discussion of the structure

Bond lengths and their e.s.d.'s are given in Table 4(*a*). The interatomic distances in the thioamido side chain have been corrected for thermal motion; Table 4(*b*) contains the corrected and uncorrected values. Bond angles and their e.s.d.'s are listed in Table 4(*c*). Table 5 lists bond lengths and angles observed in some pyridine derivatives. Fig. 1 illustrates bond lengths and angles in 2-thiopic and 4-thiopic.

Table 4. *Bond lengths and bond angles*

(*a*) Bond lengths and their e.s.d.'s (Å).

S----C(6)	1·657 (4)	C(1)–H(1)	1·00
C(6)–N(2)	1·325 (4)	C(2)–H(2)	0·99
C(6)–C(5)	1·505 (5)	C(3)–H(3)	1·02
N(1)–C(5)	1·334 (5)	C(4)–H(4)	0·99
N(1)–C(1)	1·338 (6)	N(2)–H(5)	1·01
C(1)–C(2)	1·380 (8)	N(2)–H(6)	1·00
C(2)–C(3)	1·376 (9)		
C(3)–C(4)	1·391 (7)		
C(4)–C(5)	1·386 (6)		

(*b*) Bond lengths corrected for thermal motion

	Uncorrected	Corrected
C(5)–C(6)	1·505	1·505
C(6)–S	1·657	1·674
C(6)–N(2)	1·325	1·339

(*c*) Bond angles and their e.s.d.'s (°).

S——C(6)–C(5)	122·9 (2)	H(1)–C(1)–N(1)	118
S——C(6)–N(2)	123·0 (3)	H(1)–C(1)–C(2)	119
N(2)–C(6)–C(5)	113·9 (3)	H(2)–C(2)–C(1)	122
C(6)–C(5)–C(1)	121·5 (3)	H(2)–C(2)–C(3)	119
C(6)–C(5)–N(1)	115·1 (3)	H(3)–C(3)–C(2)	124
C(5)–N(1)–C(1)	117·0 (4)	H(3)–C(3)–C(4)	129
N(1)–C(1)–C(2)	123·9 (5)	H(4)–C(4)–C(3)	120
C(1)–C(2)–C(3)	118·4 (5)	H(4)–C(4)–C(5)	122
C(2)–C(3)–C(4)	118·8 (4)	H(5)–N(2)–C(6)	119
C(3)–C(4)–C(5)	118·4 (4)	H(6)–N(2)–C(6)	120
C(4)–C(5)–N(1)	123·3 (3)	H(5)–N(2)–H(6)	121

(*a*) *Planarity in the molecule*

The details of some planes of best fit are listed in Table 6. The pyridine ring, as expected, is planar within experimental error. The S and N(2) atoms of the

Table 6. *Equations of some mean planes and displacement of atoms from these planes*

Each mean plane is represented by an equation of 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

$$0\cdot4244X+0\cdot3911Y-0\cdot8167Z-0\cdot8970=0$$

	Displacements (Å)
S	−0·2236
N(2)	0·2422
C(6)	0·0111

Pyridine ring atoms average 0·004 Å displacement.

(*b*) Thioamido side chain

$$0\cdot2545X+0\cdot4305Y-0\cdot8660Z-0\cdot4996=0$$

	Displacement (Å)
C(5)	0·0018
C(6)	−0·0057
N(2)	0·0021
S	0·0018

Table 5. *Interatomic distances and bond angles in pyridine derivatives*

	Bonds (Å)			Angles (°)			
Compound	N–C(1) N–C(5)	C(1)–C(2) C(4)–C(5)	C(2)–C(3) C(3)–C(4)	C–N–C	N–C–C	C–C–C	Literature
2-Thioamidopyridine 2-thiopic) (present compound)	1·338 1·334	1·380 1·386	1·376 1·391	117·0	123·9 123·3	118·4 118·8 118·4	This investigation
4-Thioamidopyrine (4-thiopic)	1·41 1·41	1·32 1·41	1·36 1·40	117·2	124·0 124·0	117·5 118·4 117·4	Colleter & Gadret (1967)
2-(2-Pyridylmethyldithio)-benzoic acid	1·337 1·372	1·384 1·388	1·399 1·369	118·5	123·4 120·8	117·9 119·1 120·3	Karle, Karle & Mitchell (1969)
2-(2′,4′-Dinitrobenzyl)-pyridine	1·346 1·346	1·370 1·397	1·382 1·382	117·0	125·0 122·0	117·3 119·6 119·1	Seff & Trueblood (1969)
1-Phenyl-2-(2-pyridyl) ethane-1,2-dione	1·351 1·348	1·387 1·384	1·372 1·378	116·7	122·9 123·8	118·8 118·0 119·8	Ashida, Hirokawa & Okaya (1966)
1,2-Di-(2-pyridyl)-ethane-1,2-diol	1·349 1·334	1·380 1·405	1·384 1·384	119·0	123·1 124·1	118·6 119·2 119·0	Ashida, Hirokawa & Okaya (1965)
Picolinamide	1·335 1·359	1·372 1·374	1·404 1·367	117·3	122·5 124·4	119·4 117·2 119·3	Takano, Sasada & Kakudo (1966)
Nicotinic acid	1·343 1·330	1·385 1·379	1·378 1·388	117·5	122·4 124·0	119·2 119·1 117·8	Wright & King(1953)
Pyridine (by microwave spectroscopy)	1·342 1·342	1·391 1·391	1·398 1·398	116·7	124·0 124·0	118·6 118·1 118·6	Bak, Hansen & Rastrup-Andersen (1954)

thioamido side chain are considerably displaced from the pyridine ring however and the C(6) atom of the side chain is probably significantly displaced from this mean plane.

The plane formed by the three atoms of the side chain and the C(6) atom in the pyridine ring has also been calculated. This plane together with the displacements of the atoms from the plane are listed in Table 6.

There is an angle of 10·5° between the plane through the pyridine ring and the plane of the thioamido group. Non-coplanarity in similar systems is not uncommon but the angles vary widely (Table 7). Takano, Sasada & Kakudo (1966) have suggested that non-coplanarity arises because of steric hindrance between the atoms in the side chain and the ring atoms *ortho* to the side chain. They calculated non-bonded contacts for the relevant atoms in related compounds and have shown 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 relevant data for 2-thiopic and 4-thiopic are summarized in Table 8. The S···C distances in both cases are shorter than the appropriate van der Waals contacts (C = 1·50 Å; S = 1·85 Å), and the shortest distance together with the largest angular displacement occurs in 4-thiopic. The N–N distances are closer to the expected van der Waals distance (N = 1·50 Å).

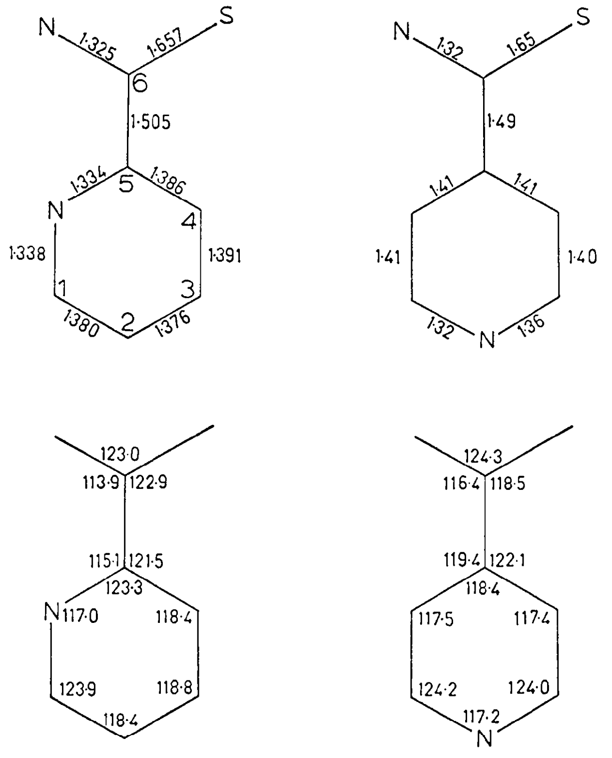

Fig. 1. Bond lengths and bond angles in 2-thiamidopyridine and 4-thiamidopyridine.

Table 8. *Non-bonded contacts in 2-thiopic and 4-thiopic*

	Contact Side chain atom	*ortho* atom	Length (Å)
2-Thiopic	S·····	CH	3·15
	N·····	NH	2·62
4-Thiopic	S·····	CH	2·96
	N·····	NH	2·75

(*b*) *Pyridine ring dimensions*

The bond lengths and angles in the pyridine ring of 2-thiopic are close to the expected values for a aromatic ring.

The ring has C–C distances of 1·383 Å with a root mean square deviation of 0·007 Å and C–N distances of 1·336 Å with a r.m.s. deviation of 0·006 Å. These compare well with the reported values from other systems, *e.g.* 1·388 and 1·342 Å (Ashida, Hirokawa & Okaya, 1965); 1·383 and 1·346 Å (Seff & Trueblood, 1968) 1·386 and 1·342 Å (Takano *et al.*, 1966). The corresponding values from 4-thiopic are 1·40 and 1·34 Å (Colleter & Gadret, 1967).

The bond angles in the ring show particularly good agreement with the microwave results from the free pyridine molecule obtained by Bak, Christenson & Rastrup-Andersen (1954).

(*c*) *Thioamido side chain dimensions*

The geometry of the thioamido side chain is undoubtedly one of the most interesting structural features of this molecule.

An unusually long (1·505 Å) C(5)–C(6) bond links the thioamido side chain with the pyridine molecule. The planarity of the side chain and the angles around C(6) indicate sp^2 orbital hybridization in that carbon atom. A pure C[sp^2]–C[sp^2] bond length should be 1·466 Å (Brown, 1959). Such a value is only expected when hetero atoms are absent. Kuchitsu, Fukuyama &

Table 7. *Interplanar angles*

	Angle between planes	Reference
Salicylamide	3°	Sasada, Takano & Kakudo (1964)
2-Thiopic	10·5	This investigation
Picolinamide	19	Takano *et al.* (1966)
Nicotinamide	28	Wright & King (1954)
Benzamide	28	Penfold & White (1959)
m-Methylbenzamide	29	Orii, Nakomura, Takaki, Sasada & Kakudo (1963)
Propyl-2-thiocarbamoyl-4-pyridine	34	Colleter *et al.*, (1970)
4-Thiopic	38	Colleter & Gadret (1967)

Morino (1968), have investigated the effect of oxygen atoms on $C[sp^2]$–$C[sp^2]$ bonds in the series butadiene, acrolein, glyoxal. Their observations show a marked lengthening of the $C[sp^2]$–$C[sp^2]$ bond as the number of oxygen atoms increase (1·463, 1·482, 1·525 Å respectively with an averaged e.s.d., *ca.* 0·001 Å). A similar effect has been observed by Takano *et al.* (1966) where the appropriate bond length for picolinamide is 1·515 Å. It is to be expected that nitrogen and sulphur atoms will have a similar but reduced effect on such bonds. The bond lengths in 2-thiopic (1·505 Å), 4-thiopic (1·49 Å) and 2-propyl-4-thiopic (1·51 Å, Colleter, Gadret & Gourselle, 1970), support this view.

Interpretations of unusually long $C[sp^2]$–$C[sp^2]$ bonds involve either a hybridization only approach (Dewar & Schmeising, 1960) or a combined approach involving hybridization, conjugation and hyperconjugation (Mulliken, 1959). Beagley, Brown & Monaghan (1969) have reviewed these approaches with respect to the C–C bond in neopentane and have concluded that changes in hybridization have only a limited effect and that the predominant factors are conjugation and hyperconjugation.

Both the C(6)–S, (1·657 Å) and the C(6)–N(2), (1·325 Å) bond lengths show significant shortening from accepted single bond values (Kitaigorodski, 1961; Trotter, 1960). Abrahams' (1956) carbon–sulphur order/length curve gives 75% double-bond character for the C(6)–S bond. In both 4-thiopic and in 2-propyl-4-thiopic (Colleter *et al.*, 1970) the corresponding values are 1·65 Å. Wheatley's (1955) carbon–nitrogen order/length curve gives approximately 30% double-bond character for the C(6)–N(2) bond length of 1·325 Å. The corresponding values in 4-thiopic (Colleter & Gadret, 1967) and in 2-propyl-4-thiopic (Colleter *et al.*, 1970) are 1·32 and 1·33 Å respectively.

The C(5)–C(6) bond length in 2-thiopic is interpreted in terms of conjugation between the thioamido side-chain and the pyridine molecule and subsequent withdrawal of electron density from the C(5)–C(6) bond into the side chain. This situation would seem to be further substantiated by the significant reduction of the C(6)–S bond (1·657 Å) in 2-thiopic compared with the 1·713 Å value in thioacetamide (Truter, 1960). In molecular orbital terms the increase in the C(5)–C(6) bond and the decrease in the C(6)–S bond lengths may be explained in terms of an increased attraction between the p_π orbital of C(5) with the C(6)–S π-bond at the expense of the C(5)–C(6), p_π–p_π interaction.

Truter has suggested that thiourea (Truter & Kunchur, 1958) and thioacetamide (Truter, 1960) correspond to purely amide forms (configuration (I) in Fig. 2). This configuration requires localization of the electron pair on the N(2) atom of the side chain and restricts the multiple bonding exclusively to the C(6)–S bond. Such a description is not consistent with the results of our investigation.

In 2-thiopic all three atoms of the side chain are involved in multiple bonding. Further evidence for the delocalization of the electron pair associated with N(2) comes from the fact that the hydrogen atoms were found to be approximately coplanar with the other atoms of the side chain and that the angles around N(2) are 120° within experimental error. Such a distribution is a strong indication for a significant contribution from configuration (II) (Fig. 2) in the overall configuration of the thioamido group. In valence bond terms an almost equal mixture of configurations (I) and (II) in Fig. 2 is expected. A qualitative molecular orbital approach may also account for the delocalization of the four π electrons of the side chain. The molecular orbitals being formed from the p_z atomic orbitals of N(2), C(6) and presumably the sulphur atom, although *d* orbital participation in the latter case cannot be entirely excluded.

Colleter & Gadret also consider the thioamide group to be conjugated to the pyridine molecule in 4-thiopic and that the bonding in the thioamide group is not purely amide in form.

(*d*) *Molecular packing and hydrogen bonding*

Fig. 3 illustrates the molecular packing viewed down the *a** axis. The shortest (less than 4·0 Å) non-bonding contacts are listed in Table 9.

The packing diagram shows layers of molecules lying mainly parallel to the (*b*,*c*) plane and stacked in the direction of the *a* axis. The nearest contact between non-hydrogen atoms in neighbouring molecules is the 3·43 Å distance which connects the thioamido sulphur and N(2) nitrogen atoms *via* a hydrogen atom across symmetry centres. Although this contact is slightly longer than the sum of the van der Waals radii of these

Amide form (I) Ionic form (II)

Fig. 2. Canonical forms of the thioamido group.

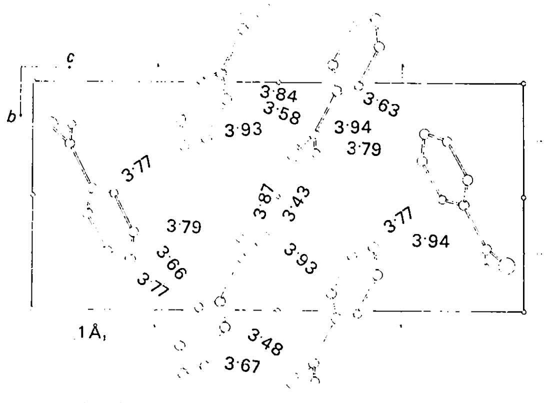

Fig. 3. 2-Thiamidopyridine packing diagram. Projection along *a**.

Table 9. *Shortest non-bonding intermolecular contacts in 2-thioamidopyridine*

Equivalent position	Symmetry code
x,y,z	1
x,y,z	2
$x,\frac{1}{2}+y,\frac{1}{2}-z$	3
$x,\frac{1}{2}-y,\frac{1}{2}+z$	4

Atom *A*	Atom *B*	Symmetry code	Cell	Length
S*	N(2)	2	1,0,0	3·43 Å
C(4)	N(2)	2	1,1,0	3·48
C(4)	C(6)	2	1,1,0	3·58
C(5)	C(6)	3	1,0,0	3·63
C(1)	N(1)	3	1,0,0	3·66
C(3)	N(2)	2	1,1,0	3·67
C(2)	N(1)	3	1,0,0	3·77
C(1)	N(2)	3	1,0,0	3·79
C(5)	C(5)	2	1,1,0	3·84
S	S	2	0,0,0	3·87
C(3)	C(6)	2	1,1,0	3·93
S	C(4)	2	1,1,0	3·93
C(6)	C(2)	3	1,1,0	3·94

* hydrogen bond N(2)–H...S

atoms (N=1·50; S=1·85 Å; Pauling, 1960) it is similar to other reported values (Table 10). Location of the hydrogen atom positions in 2-thiopic has shown the N–H···S bond to be linear, within experimental, error, and the S···H distance to be 2·4 Å. This latter value indicates that sulphur and hydrogen atoms do interact significantly in the N–H···S bonds in 2-thiopic with a shortening of the van der Waals radii for these atoms of approximately 0·6 Å.

Hamilton & Ibers (1968) have discussed the role of sulphur as a hydrogen bond acceptor and have pointed out the possible importance of N–H···S bonds in biological systems. Of particular relevance to this report are the comments of Valle, Cojazzi, Busetti & Mammi (1970) that the doubts about the possible existence of hydrogen bonds of the type N–H···S with dimensions in the range listed in Table 10, (3·3 to 3·5 Å) are largely due to uncertainties in the van der Waals radii for sulphur. The location of the hydrogen atoms in the structure reported by Valle *et al.* (1970, Table 10) in this structure and in propyl-2-thiocarbamoyl-4-pyridine (Colleter *et al.*, 1970) should assist in establishing the existence of hydrogen bonds of the type already discussed and with distances in the range 3·3 to 3·5 Å.

The close similarities between 2-thiopic and 4-thiopic extend to the manner in which the molecules are packed in the crystal. The essential similarities being the layering of hydrogen-bonded dimers in the (*b*,*c*) plane and the stacking of these dimers in the direction of the *a* axis. An important different between the structure is the existence of a hydrogen bond (2·90 Å) of the type N–H···N between the amido nitrogen and the pyridine nitrogen of neighbouring molecules in 4-thiopic. This bond is a result of the thioamido group occupying the *para* position, relative to the pyridine nitrogen atom, in 4-thiopic; consequently, a similar bond would not be expected in 2-thiopic. All calculations were performed on an IBM 1620 computer in the Department of Mathematics, Statistics and Computing, Newcastle-upon-Tyne Polytechnic.

We are grateful to Professor R. Shiono of the Crystallography Laboratory University of Pittsburgh, Pennsylvania and Dr F. R. Ahmed of N.R.C., Ottawa,

Table 10. *Intermolecular* N–S *distances*

N–H...S distance (Å)	Molecule	Reference
3·44	Ethylenethiourea	Wheatley (1953)
3·48		
3·26	α-Thiopyridine	Penfold (1953)
3·42	Thiourea	Truter & Kunchur (1958)
3·40	2,5-Diamino-4-mercapto-6-methylpyrimidine	Maslen, Jakes & Clews (1958)
3·24	3-Hydro-5-thiol-1,2,4-triazole	Senko & Templeton (1958)
3·396	Thioacetamide	Truter (1960)
3·420		
3·469		
3·504		
3·35	Xanthane hydride	Stanford (1963)
3·30	Trimethylenethiourea	Dias & Truter (1964)
3·366	Pyridaz-3-thione	Hossain & Carlisle (1966)
3·44	4-Thioamido pyridine	Colleter & Gadret (1967)
3·38	Hydrazinium hydrazinedithiocarboxylate	Braibanti, Manotti Lanfredi, Tiripicchio & Loquidice (1969)
3·30	Thiosemicarbazine	Domiano, Fava Gasparri, Nardelli & Sgarabotto (1969)
3·41		
3·409	1-Thiocarbamyl-imidazolidine 2-Thione	Valle *et al.*, (1970)
3·449		
3·39	Propyl-2-thiocarbamoyl-4-pyridine (2 propyl-4-thiopic)	Colleter *et al.*, (1970)
3·43	2-Thioamidopyridine	This investigation

Canada for supplying the following programs which were used in the analysis.

Professor Shiono supplied: data reduction, structure factor calculations, Fourier summation, inter and intramolecular distance calculation and bond lengths and angles calculation. Dr F. R. Ahmed supplied the structure factors, least-squares, (block-diagonal approximation) program (author: G. A. Mair).

Thanks are due to Mr R. Fleeting and the computing staff of the Newcastle-upon-Tyne Polytechnic for assisting us with the computing.

We wish to express our thanks to Dr G. J. Sutton of the University of New South Wales, Australia for supplying us with the compound and to the Governors of the former Rutherford College of Technology, Newcastle upon Tyne for the provision of a research grant to W. H.

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