

### 3-Thioxo-2-pyridinecarboxylic Acid, C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>S. Redetermination of the Structure

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**Abstract.**  $M_r = 155.17$ , monoclinic,  $P2_1$ ,  $a = 10.498$  (2),  $b = 7.119$  (1),  $c = 4.3216$  (8) Å,  $\beta = 96.18$  (2)°,  $U = 321.10$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.604$  Mg m<sup>-3</sup>, graphite-monochromated Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 0.422$  mm<sup>-1</sup>,  $T = 298$  K. Final  $R = 0.029$  for 1116 independent reflections. The molecule is shown to be present in the crystal in the thione-acid form with a H atom bonded to the pyridine N atom. This conflicts with the findings of Dereppe, Schanck, Declercq, Germain & Van Meerssche, [*Bull. Soc. Chim. Belg.* (1976). **85**, 729–733] where the molecule was presented in the thiol-acid form with no exocyclic substituent on the ring N atom.

**Introduction.** Some time ago we determined the crystal structure of 3-thioxo-2-pyridinecarboxylic acid from two-circle diffractometer data, but later found that the structure had been completed and published by Dereppe, Schanck, Declercq, Germain & Van Meerssche (1976). These authors presented the molecule in the thiol-acid form with no exocyclic substituent on the ring N atom. It was evident that in this respect the structure proposed by them was probably incorrect, for the internal ring angle at the N atom of 123.5 (2)° obtained by them is consistent with there being a substituent at that position (when there is no substituent, the internal ring angle is usually 4–6° smaller than this value), and when this N atom has a H atom [H(1)] attached to it, it can form a normal hydrogen bond to a carboxyl O atom of a neighbouring molecule. When H(1) is considered to be bonded to the S atom, as in the structure proposed by Dereppe *et al.* (1976), it does not take part in hydrogen bonding nor is its position entirely consistent with the length of the C–S bond. The H atom in question was located by Dereppe *et al.* (1976) in a difference Fourier map. Our determination indicated that the H atom was bonded to the ring N atom, but our data were clearly not as good as those of Dereppe *et al.* (1976) and the matter was shelved.

Renewed interest in the compound as a therapeutic agent (Berkoff, 1981) and the acquisition of a CAD-4 diffractometer have prompted us to collect a new data set and to refine the structure again. The results of this refinement are presented here.

**Experimental.** The sample was a gift from SmithKline Beckman (SK&F No. 34288); CAD-4 diffractometer was used; crystal dimensions 0.04 (1) × 0.27 (1) × 0.15 (1) mm; unit-cell parameters obtained do not differ significantly from those of Dereppe *et al.* (1976); a total of 1284 intensities measured in two quadrants ( $\pm k$ ,  $2\theta_{\max} = 50^\circ$ ),  $\omega/2\theta$  scan technique, averaged (where appropriate) in point group 2 to give a set of 1116 independent data; measured intensities of three periodically monitored standard reflections did not show any significant variation as a function of time, absorption corrections not applied; full-matrix least squares, minimizing  $\sum w(\Delta F)^2$  where  $w = \sigma^{-2}(|F_o|^2)$ , starting from parameters of Dereppe *et al.* (1976) for all atoms except H(1), all intensity data used in refinement, scattering factors for S, O, N, C and H taken from *International Tables for X-ray Crystallography* (1974), curve used for H calculated by Stewart, Davidson & Simpson (1965), correction made for real and imaginary parts of anomalous dispersion of S (Cromer & Liberman, 1970); parameters refined included a scale factor, positional and anisotropic temperature factor coefficients for non-H and positional and isotropic thermal parameters for H,  $F(000) = 160$ .

The first refinement sequence did not include H(1). The most prominent feature in a difference Fourier map calculated at the end of this sequence was a peak near N(1) at the expected site for a H atom. Further refinement with H(1) at this site converged satisfactorily (av. shift/error = 0.0001, max. shift/error = 0.01). The highest positive region in a final difference Fourier map was less than 0.2 e Å<sup>-3</sup>. An isotropic extinction parameter was included in the refinement initially, but did not influence the structural parameters significantly, and was omitted in the final refinement.

Refinement of the two enantiomorphic models gave  $wR = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2)^2]^{1/2} = 0.047$  and 0.052. The former is significant at the 0.005 level (Hamilton, 1965). Final atomic coordinates for the

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Table 1. Atomic coordinates and isotropic thermal parameters

The *y* coordinate of S(3) was not varied during the refinement. H-atom temperature factors =  $\exp[-B \sin^2\theta/\lambda^2]$ .  $B_{eq}$  is defined by Willis & Pryor (1975).

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}/B(\text{\AA}^2)$
N(1)	0.8311 (2)	-0.4402 (3)	0.7232 (5)	2.75
C(2)	0.8139 (2)	-0.6090 (3)	0.5811 (5)	2.36
C(3)	0.7075 (2)	-0.6393 (3)	0.3646 (5)	2.58
S(3)	0.6786 (1)	-0.8471	0.1632 (2)	3.82
C(4)	0.6221 (2)	-0.4875 (4)	0.3128 (7)	3.31
C(5)	0.6429 (2)	-0.3206 (4)	0.4638 (7)	3.70
C(6)	0.7515 (2)	-0.2969 (3)	0.6723 (7)	3.38
C(7)	0.9172 (2)	-0.7467 (3)	0.6912 (6)	2.83
O(1)	0.9144 (2)	-0.9091 (2)	0.5501 (5)	3.71
O(2)	0.9984 (2)	-0.7075 (3)	0.8990 (4)	4.01
H(1)	0.905 (2)	-0.425 (4)	0.871 (6)	3.9 (6)
H(4)	0.544 (2)	-0.496 (4)	0.138 (6)	4.5 (7)
H(5)	0.584 (2)	-0.213 (4)	0.404 (6)	3.9 (6)
H(6)	0.772 (2)	-0.197 (4)	0.796 (6)	4.2 (7)
H(O1)	0.840 (2)	-0.918 (4)	0.387 (7)	6.1 (8)

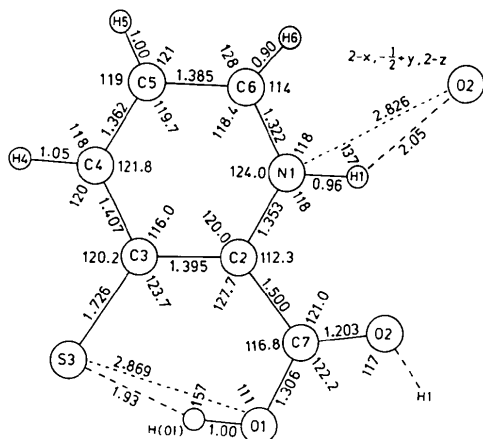


Fig. 1. Interatomic distances (Å) and angles (°). Standard deviations are: C—C(N,O), 0.004; C—S, 0.003; H—C (N), 0.04 Å; and 0.2° in angles not involving H, 2.5° in the remainder.

model with  $wR = 0.047$  are listed in Table 1.\* Atom labelling, bond lengths and angles are shown in Fig. 1. Computer programs used in this analysis were locally modified version of programs from a variety of sources (Taylor, 1973).

**Discussion.** The refined parameters obtained here are in very good agreement with those of Dereppe *et al.* (1976); all non-H atomic coordinates are within  $2\sigma$  of

each other except for the *z* coordinates of N(1) ( $4\sigma$ ) and C(7) ( $5\sigma$ ). The H-atom coordinates, with the obvious exception of H(1), and all thermal parameters are also in reasonable agreement. The value for the angle C(2)—N(1)—C(6) of 124.0 (2)° does not differ significantly from the value of 123.5 (2)° given by Dereppe *et al.* (1976). This measure of agreement leaves no doubt that the two sets of results were obtained from the same crystalline substance, and not, for example, from different tautomers. The structure proposed by Dereppe *et al.* (1976) is, therefore, incorrect in that the H atom in question which is bonded to the N atom had been located near the S atom in their paper.

The intermolecular hydrogen bond between N(1) and O(2) of an adjacent molecule is shown in Fig. 2 and the dimensions associated with this bond in Fig. 1. There is also an intramolecular hydrogen bond O(1)—H(O1)···S(3). Thus, both H atoms that would be expected to take part in hydrogen-bond formation do so. The intramolecular hydrogen bond is very short and it seems that the angles C(2)—C(3)—S(3) of 123.7 (2)° and C(3)—C(2)—C(7) of 127.7 (2)° are distorted from their more normal values to accommodate this bond, e.g. the corresponding angles in 3,3'-dithiodi-2-pyridinecarboxylic acid (Chaikum & Taylor, 1980), where no such hydrogen bond is found, are 120.6 (2) and 121.0 (2)° and the O···S non-bonded separation is 2.683 (4) Å [*cf.* 2.869 (3) Å here]. In salicylic acid (Sundaralingam & Jensen, 1965), where an intramolecular hydrogen bond is present, the corresponding parameters are 122.7, 120.4° and 2.620 Å, indicating that with O in place of S the intramolecular hydrogen bond can exist without the distortion observed here. The centres of the atoms of the six-membered ring incorporating this hydrogen bond lie close to the same plane; deviations from the least-squares plane through C(2), C(3), C(7), O(1) and S(3) range from -0.041 (3) to +0.021 (3) Å, while H(O1) is only 0.08 (4) Å from this plane.

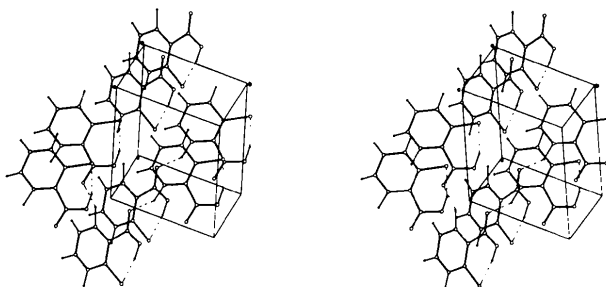
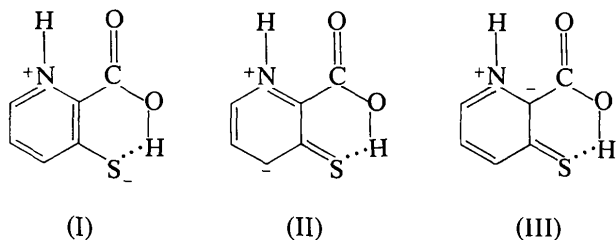


Fig. 2. A stereoscopic diagram of the structure drawn by VIEW (Carrell, 1979). Hydrogen bonds are shown as dashed lines. The axial system is right-handed with the positive direction of the *c* axis towards the viewer and to the left and the *b* axis towards the viewer and to the right, with the origin at the top of the diagram.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38124 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The plane of the carboxyl group [C(2), C(7), O(1), O(2)] is tilted at an angle of  $4.1(3)^\circ$  to the least-squares plane of the six atoms of the pyridine ring. The pyridine ring shows marked, but barely significant, deviations from planarity: deviations from the plane through N(1), C(2), C(3), C(4), C(5) and C(6) are  $0.002(3)$ ,  $-0.005(3)$ ,  $0.004(3)$ ,  $-0.002(3)$ ,  $-0.008(3)$  and  $0.009(3)$  Å respectively. This distortion probably results from the strain imposed on the system in opening the exocyclic angles at C(2) and C(3) to accommodate the intramolecular hydrogen bond.

The C(3)—S(3) bond length lies between that expected for a single bond associated with a conjugated system, e.g.  $1.783(4)$  Å in 3,3'-dithiodi-2-pyridinecarboxylic acid (Chaikum & Taylor, 1980), and that expected for a double bond. This fact, and the other bond lengths in the molecule, suggest that (I) is a significant contributor to the resonance hybrid. (II) and (III) are also important with the negative charge shown on C(2) probably being delocalized over the carboxyl group O atoms.



The molecular structure is, therefore, similar to those of the 2,4- (Declercq, Schanck, Germain, Dereppe & Van Meerssche, 1977) and the 2,6-isomers (Germain,

Declercq, Schanck, Dereppe & Van Meerssche, 1977) in that the N atom of the pyridine ring is protonated, but different in that in the 2-isomers the adjacent N atom constrains the C—S bond to have more double-bond character. Canonical forms like (I) make smaller contributions to these 2-isomers.

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## Structure of Funicin,\* Antimicrobial Substance from *Aspergillus funiculosus*, C<sub>17</sub>H<sub>18</sub>O<sub>5</sub>

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**Abstract.**  $M_r = 302.4$ , triclinic,  $P\bar{1}$ ,  $a = 11.147(5)$ ,  $b = 7.388(4)$ ,  $c = 10.551(4)$  Å,  $\alpha = 106.01(6)$ ,  $\beta =$

$107.77(6)$ ,  $\gamma = 101.27(6)^\circ$ ,  $V = 757.4$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.33$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 0.82$  mm<sup>-1</sup>,  $T = 293$  K. Final  $R = 0.049$  for 1844 unique reflections. The dihedral angle between the two phenyl rings is  $64^\circ$ . An intramolecular hydrogen bond O(4)—H(17)···O(1) is formed between hydroxyl and

\* Ethyl 2-hydroxy-4-(3-hydroxy-5-methylphenoxy)-6-methylbenzoate.

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