

2-Thiopyridone: X-ray and Neutron Diffraction Study

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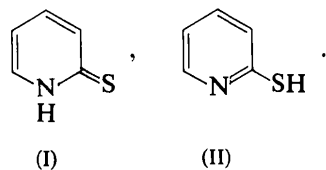
Abstract

2-Thiopyridone, C_5H_5NS , is monoclinic, space group $P2_1/c$ with $a = 6.107(2)$, $b = 6.325(2)$, $c = 14.382(4)$ Å, $\beta = 103.0(5)^\circ$, $Z = 4$. Penfold's [*Acta Cryst.* (1953). **6**, 707–713] determination of the crystal structure ($R = 0.10$) was confirmed, but the existence of the tautomeric thione form can now be unequivocally proved by the much higher accuracy of the present parameters ($R = 0.029$ for 884 independent X-ray data, $R = 0.023$ for 949 independent neutron data) and by locating the H atoms.

Introduction

The crystal structure of 2-thiopyridone has already been determined by Penfold (1953) with photographic methods ($R = 0.10$). From the length of the C–S bond (1.68 Å), Penfold concluded that the molecule occurs in the crystal in the tautomeric pyridinethione form (I) instead of in the alternative thiol form (II).

Our reinvestigation was performed to derive more accurate parameters and to locate unequivocally the positions of the H atoms, and thus to confirm (or disprove) Penfold's conclusion. Another aim of this investigation is to provide a preliminary study of the deformation density in the molecule at room temperature. It will be followed by a (more accurate) study at 120 K. For this temperature the crystal structure has already been verified to be the same, by means of Guinier exposures down to 100 K.



X-ray investigation

Experimental

A single crystal grown from an ethanolic solution ($0.5 \times 0.35 \times 0.25$ mm) was mounted onto a thin

quartz thread and coated with paraffin in order to prevent the slow evaporation of the substance. An automatic four-circle diffractometer (Fa. Stoe) was used to measure the intensities of all symmetrically equivalent reflections up to $2\theta = 55^\circ$ with an integral method (Mo $K\alpha$, graphite monochromator). The lattice constants were determined from the 2θ positions of 20 reflections by least-squares refinement. As much as was allowed by the geometry of the diffractometer, each reflection was additionally measured in two ψ positions of $\pm 5^\circ$ in order to improve the accuracy and to check on multiple reflection (*Umweganregung*). 11142 intensities were measured altogether; the internal R values for the symmetry-equivalent and ψ -equivalent reflections were $R_I = 0.033$ for the observed reflections, and $R_I = 0.039$ for all reflections. With $\mu = 4.6 \text{ cm}^{-1}$ an absorption correction was superfluous. After Lorentz and polarization corrections were applied, the averaging procedure over the equivalent reflections yielded 1224 independent reflections, 884 of which were classified as observed [$I \geq 2\sigma(I)$].

Refinement

Penfold's (1953) parameters were transformed into the standard setting $P2_1/c$, and were used as a starting set. Scattering factors for the H, C, N and S atoms were taken from *International Tables for X-ray Crystallography* (1974). Anomalous scattering of the S atom was corrected only in the real part of the scattering factor ($f' = 0.110$; *International Tables for X-ray Crystallography*, 1974) because the structure is centrosymmetric. Anisotropic thermal parameters were used except for the H atoms. Weights were taken as $w = 1/\sigma^2(F_o)$. With 84 parameters, we finally obtained for the 884 observed reflections $R = 0.029$, $R_w = 0.004$, g.o.f. = 0.34, and for all 1224 reflections $R = 0.048$, $R_w = 0.006$, g.o.f. = 0.49. The inclusion of an isotropic extinction parameter did not lead to a significant improvement. Final coordinates and isotropic temperature factors are given in Table 1,* bond lengths and

* Lists of structure factors and anisotropic thermal parameters β_{ij} have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36389 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters for 2-thiopyridone in lattice units, and equivalent isotropic temperature factors

X denotes the X-ray investigation, *N* the neutron investigation.

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} g_{ij}, \text{ where } g_{ij} \text{ is the metric tensor.}$$

		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
S	<i>X</i>	0.3330 (1)	0.4370 (1)	0.0927 (1)	4.54 (2)
	<i>N</i>	0.3331 (3)	0.4373 (3)	0.0929 (1)	4.50 (8)
N	<i>X</i>	-0.0576 (2)	0.2375 (2)	0.0707 (1)	3.67 (5)
	<i>N</i>	-0.0578 (1)	0.2378 (1)	0.07062 (4)	3.69 (2)
C(1)	<i>X</i>	0.1642 (3)	0.2390 (3)	0.1138 (1)	3.35 (6)
	<i>N</i>	0.1636 (1)	0.2388 (1)	0.11386 (4)	3.42 (3)
C(2)	<i>X</i>	0.2386 (3)	0.0648 (3)	0.1748 (1)	4.26 (7)
	<i>N</i>	0.2387 (1)	0.0650 (1)	0.17464 (5)	4.33 (4)
C(3)	<i>X</i>	0.0929 (4)	-0.0940 (3)	0.1859 (1)	4.87 (8)
	<i>N</i>	0.0934 (1)	-0.0941 (1)	0.18582 (6)	4.97 (4)
C(4)	<i>X</i>	-0.1333 (4)	-0.0854 (3)	0.1385 (1)	4.94 (8)
	<i>N</i>	-0.1342 (1)	-0.0859 (1)	0.13818 (2)	5.04 (4)
C(5)	<i>X</i>	-0.2036 (3)	0.0832 (3)	0.0817 (1)	4.32 (7)
	<i>N</i>	-0.2040 (1)	0.0842 (1)	0.08123 (6)	4.40 (4)
H(2)	<i>X</i>	0.4067 (30)	0.0586 (30)	0.2066 (8)	3.75 (51)
	<i>N</i>	0.4137 (4)	0.0612 (4)	0.2124 (2)	5.70 (12)
H(3)	<i>X</i>	0.1693 (33)	-0.2254 (35)	0.2301 (15)	2.41 (42)
	<i>N</i>	0.1571 (4)	-0.2272 (4)	0.2322 (2)	10.45 (10)
H(4)	<i>X</i>	-0.2530 (31)	-0.2070 (33)	0.1419 (15)	3.96 (51)
	<i>N</i>	-0.2511 (5)	-0.2097 (4)	0.1458 (2)	9.52 (12)
H(5)	<i>X</i>	-0.3430 (36)	0.1106 (32)	0.0455 (13)	4.51 (54)
	<i>N</i>	-0.3760 (4)	0.1120 (4)	0.0436 (2)	4.93 (12)
H(N)	<i>X</i>	-0.1181 (37)	0.3405 (28)	0.0278 (14)	2.55 (36)
	<i>N</i>	-0.1204 (3)	0.3615 (3)	0.0245 (1)	4.61 (11)

angles in Fig. 1. For the thermal parameters Hirshfeld's (1976) rigid-bond test was calculated (Table 2). Since values of ΔU (bond direction) ≤ 0.0010 Å are expected for bonds not involving hydrogen, the results are satisfactory.

Since the ring atoms of the molecule appear to form essentially a rigid body, a refinement of the rigid-body vibration tensors TLS proved to be successful. The three diagonal libration components, referred to a Cartesian reference system, are 27.1, 25.6 and 18.8 (°)² with e.s.d.'s of 3.8, 4.0 and 1.6 (°)². With the libration tensor thus obtained, we calculated corrections for bond lengths and angles (Scheringer, 1978); they range from 0.0060 to 0.0102 Å and from -0.079 to 0.111° respectively.

Neutron investigation

Experimental

A C₅H₅NS crystal of approximately 85 mm³ was used for the neutron diffraction investigation performed on the automatic four-circle diffractometer P32 at the research reactor FR2 Kernforschungszentrum Karlsruhe. A neutron wavelength $\lambda_n = 1.0202$ Å was obtained with a vertical-focusing Cu(311) monochromator. The lattice parameters were determined from a point-of-gravity adjustment of 20 selected

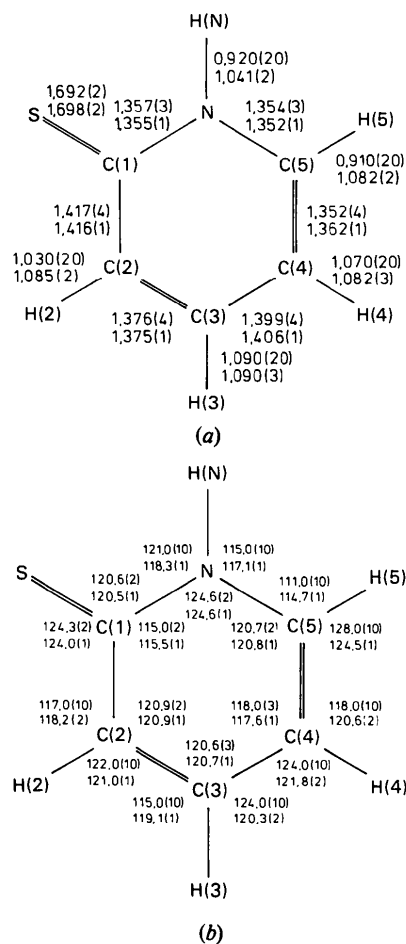


Fig. 1. (a) Bond lengths (Å) and (b) bond angles (°) in the molecule. The upper value refers to the X-ray investigation, the lower value to the neutron investigation.

Table 2. Rigid-bond test for the thermal parameters

The table contains the absolute values of the differences of the vibration components of the respective atoms in the direction of the bonds (Å² × 10⁴).

	C(1)- C(2)	C(2)- C(3)	C(3)- C(4)	C(4)- C(5)	C(5)- N	N- C(1)
<i>X</i>	13	3	6	8	0	13
<i>N</i>	10	6	13	8	2	5

	C(1)- S	S(2)- H(2)	C(3)- H(3)	C(4)- H(4)	C(5)- H(5)	N- H(N)
<i>X</i>	16	247	62	1	218	83
<i>N</i>	16	54	75	40	51	67

reflections; they are $a = 6.113$ (5), $b = 6.325$ (5), $c = 14.400$ (9) Å, $\beta = 103.1$ (1)°. The intensities of 2574 reflections up to $\sin \theta/\lambda = 0.63$ Å⁻¹ were measured with the ω -step scan method. Because of the large incoherent neutron scattering of hydrogen, an absorption correction was performed with a linear

absorption coefficient of $\mu = 2.0 \text{ cm}^{-1}$; the program of Wuensch & Prewitt (1965) was used. Averaging over symmetrically equivalent reflections yielded 1080 independent reflections, 840 of which were classified as observed [$I \geq 2\sigma(I)$]; the internal reliability value for all equivalent reflections was $R_i = 0.02$.

Refinement

Full-matrix least-squares refinement was started with the parameters from the X-ray refinement. Scattering lengths were taken from Koester (1977): 9.36(N), 6.648(C), 2.847(S) and $-3.741(\text{H})$ (all values in fm). Atomic coordinates, anisotropic temperature factors, a scale factor and an extinction parameter (110 parameters) were refined with the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Weights were taken as $w = 1/\sigma^2(F_o)$. Final coordinates and isotropic temperature factors are given in Table 1,* bond lengths and angles in Fig. 1. The isotropic extinction parameter was $g = 1.43(3) \times 10^{-4}$. We reached final reliability values $R(F) = 0.027$ and $R_w(F) = 0.023$ for 949 contributing reflections (unobserved reflections, but with $F_c > F_o$, were also considered as contributing reflections), and g.o.f. = 1.43. Rigid-bond test values (Hirshfeld, 1976) were calculated and are given in Table 2; the results are satisfactory, even for the bonds involving H atoms.

Comparison of X-ray and neutron parameters

The average over the absolute values of the differences between the two sets of positional parameters are 0.0024, 0.0023 and 0.0031 Å for the x , y , and z directions respectively (H atoms being excluded). The e.s.d.'s obtained in the refinement range from 0.0006 to 0.0025 Å, but are underestimated by a factor of about 1.56, as indicated by the actual slope of the normal probability plot (Abrahams & Keve, 1971), see Fig. 2(a). The differences between the two sets of param-

eters fall nearly into the error limits and departure from linearity in the plot (Fig. 2a) is only slight; thus, we conclude that the differences between the positional parameters are in the main of random nature. For the thermal parameters U_{11} , U_{22} , U_{33} , U_{12} , U_{13} , U_{23} the absolute values of the differences are 0.0021, 0.0025, 0.0025, 0.0009, 0.0012 and 0.0029 Å² respectively, whereas the e.s.d.'s (also underestimated by a factor of about 1.67 as indicated by the actual slope of the half-normal plot) range from 0.0003 to 0.0017 Å². Here the differences between the two sets of parameters are a little larger than the e.s.d.'s and are also larger than one would expect from the good results of the rigid-bond test (Table 2). Departure from linearity in the half-normal plot for the thermal parameters (Fig. 2b) is about as large as in the plot for the positional parameters (Fig. 2a) and thus does not convincingly show systematic differences between the two sets of thermal parameters. They may, however, be present due to the fact that, in the X-ray refinement, the thermal parameters can be falsified by the presence of bonding density. Furthermore, we have calculated χ^2 tests (Hamilton, 1969) for the two sets of parameters and, without further discussion, we give only the relevant figures: for the 21 positional parameters we obtain $\chi_{\text{exp}}^2 = 53.7$, $\chi_{\text{exp}}^2(\text{scaled}) = 22.0$ and the theoretical value $\chi^2(21, 0.001) = 46.8$. For the 42 thermal parameters we obtain $\chi_{\text{exp}}^2 = 115.6$, $\chi_{\text{exp}}^2(\text{scaled}) = 41.5$ and $\chi^2(42, 0.001) \approx 75$.

The configuration of the molecule

The molecule is essentially planar. The S atom deviates from the mean plane through the six ring atoms by 0.005 Å, and the H atoms deviate by at most 0.06 Å.

By analogy with 2-pyridone and from the length of the C—S bond (1.68 Å), Penfold (1953) concluded that the molecule occurs in the crystal in the tautomeric thione form (I). We can now present three further arguments to confirm this conclusion: (1) Our neutron (and even our X-ray) investigation has clearly shown that the H atom is attached to the N atom and not to the S atom. (2) The angle at the N atom in the ring is 124.6(2)°. In all pyridine derivatives where the N atom is protonated, this angle is always greater than 120° (Kvick & Booles, 1972). On the other hand, all pyridine derivatives which are not protonated at the N atom have angles less than 120°. (3) The bond lengths in the ring are found to be different and thus allow us to distinguish between single and double bonds. Since the thiol form (II) is aromatic, we would expect to find essentially equal bond lengths for this form, whereas the different lengths actually suggest the (non-aromatic) thione form (I).

The packing of the molecules in the crystal is as described by Penfold (1953). Two molecules are linked

* See deposition footnote.

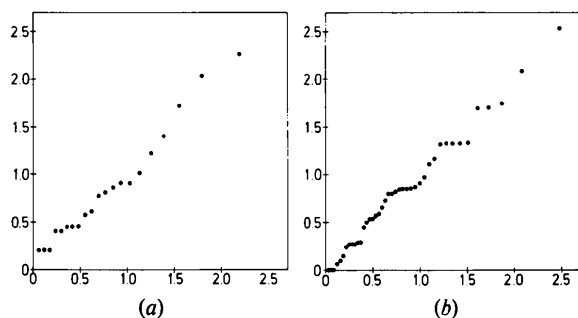


Fig. 2. Half-normal probability plots for the observed differences between X-ray and neutron parameters. Hydrogen parameters are not included. The slope has been scaled to unity. (a) Positional parameters. (b) Thermal parameters.

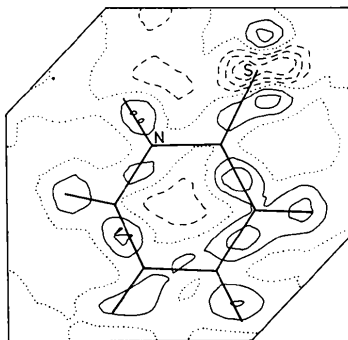


Fig. 3. $X-N$ map for 2-thiopyridone at 293 K. Contour interval: $0.1 \text{ e } \text{\AA}^{-3}$. Positive density: full lines; zero density: dotted lines; negative density: dashed lines.

to each other by two $N-H \cdots S$ hydrogen bonds through a crystallographic centre of symmetry. For the distance $N-S$ we found $3.289(2) \text{ \AA}$, and for the angle at H, 164° . Thus, the hydrogen bond is bent.

The $X-N$ map, shown in Fig. 3, gives a first impression of the deformation density in the molecule. Since thermal smearing is large at room temperature, the bond peaks are not very high ($0.15\text{--}0.25 \text{ e } \text{\AA}^{-3}$) and a little irregular. The pronounced non-spherical minimum of $-0.35 \text{ e } \text{\AA}^{-3}$ at the S atom, with the accompanying peaks at either side, is probably due to a discrepancy in the thermal parameters of the S atom, as derived from the X-ray and neutron data. The β_{11} and β_{22} components of the S atom each differ by about 5% of their magnitude, whereas the β_{33} com-

ponents are nearly equal. This discrepancy (referring only to two directions of space) indicates that the neutron parameters β_{11} and β_{22} do not fit well to the X-ray data and, hence, cause a systematic error in the representation of the electron-density distribution ($X-N$ map).

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Structures of Two Sesquiterpene Lactones: Argophyllin-A and (8S)-Methacryloxy 1,10;4,5-diepoxykostenolide

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Abstract

Argophyllin-A (1a), $C_{20}H_{28}O_7$ ($M_r = 380.44$), isolated from *Helianthus argophyllus*, and (8S)-methacryloxy-1,10;4,5-diepoxykostenolide (2), $C_{19}H_{24}O_6$ ($M_r = 348.4$), isolated from *Vernonia jonesii*, are germacranolide-type sesquiterpene lactones. The space

group for both compounds is $P2_12_12_1$, with $a = 11.506(4)$, $b = 17.273(5)$, $c = 9.999(4) \text{ \AA}$, $Z = 4$, $V = 1987(1) \text{ \AA}^3$, $d_c = 1.272 \text{ Mg m}^{-3}$ for (1a) and $a = 12.296(2)$, $b = 18.595(4)$, $c = 7.735(1) \text{ \AA}$, $Z = 4$, $V = 1769.6(7) \text{ \AA}^3$, $d_c = 1.308 \text{ Mg m}^{-3}$ for (2). The structures were solved by direct methods and refined by a full-matrix least-squares technique to final R values of 0.060 and 0.068 utilizing 1760 and 1779 reflexions, respectively. Thermal parameters for the nonhydrogen

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