

5*H*-1-Benzothiopyrano[2,3-*b*]pyridin-5-one

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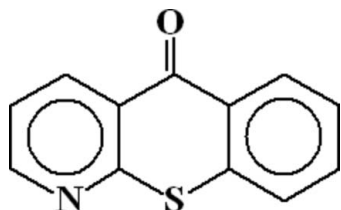
Received 23 July 2008; accepted 31 July 2008

Key indicators: single-crystal X-ray study; *T* = 296 K; mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$; disorder in main residue; *R* factor = 0.071; *wR* factor = 0.180; data-to-parameter ratio = 14.3.

Molecules of the title compound, $\text{C}_{12}\text{H}_7\text{NOS}$, with one half-molecule in the asymmetric unit, are disordered about a crystallographic centre of inversion. Refinement showed that the C=O group is disordered with the S atom and the N atom is disordered over four positions. Adjacent molecules are connected through C—H \cdots O hydrogen bonds and $\pi\cdots\pi$ interactions (centroid-centroid distances of 3.635 and 3.858 \AA).

Related literature

For related literature, see: Hidetoshi (1997); Khan *et al.* (2008); Mann & Reid (1952).



Experimental

Crystal data

$\text{C}_{12}\text{H}_7\text{NOS}$
M_r = 213.26
Monoclinic, $P2_1/c$
a = 7.7308 (18) \AA
b = 3.8585 (9) \AA
c = 15.771 (3) \AA
 β = 99.333 (9) $^\circ$
V = 464.20 (18) \AA^3
Z = 2
Mo $K\alpha$ radiation
 μ = 0.31 mm^{-1}
T = 296 (2) K
0.25 × 0.06 × 0.04 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.977, *T_{max}* = 0.987
5384 measured reflections
1189 independent reflections
822 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.070$
wR(F^2) = 0.179
S = 1.17
1189 reflections
83 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.62 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C5—H5 \cdots O1 ⁱ	0.93	2.53	3.286 (7)	139

Symmetry code: (i) $x, -y - \frac{1}{2}, z - \frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

The authors acknowledge the Higher Education Commission, Islamabad, Pakistan, for funding the purchase of the diffractometer at GCU, Lahore.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2756).

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supplementary materials

Acta Cryst. (2008). E64, o1704 [doi:10.1107/S1600536808024628]

5*H*-1-Benzothiopyrano[2,3-*b*]pyridin-5-one

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Comment

In continuation of our studies of pyridine containing heterocyclic compounds (Khan, *et al.*, 2008), the title compound has been synthesized. As the molecule is located on a centre of inversion the thio (S1) and carbonyl group (C6=O1) are disordered over two sites with 50% occupancy. For the N atom four different positions were found with an occupancy factor of 0.25. Adjacent molecules are linked to each other through intermolecular H-bonding of C—H···O type (Table 1). In addition, there are $\pi\cdots\pi$ -interactions between the adjacent molecules. The centroid of the ring composed by C1, C2, C3A, C4, C5, and N1B is at 3.635Å from the centroid of the central ring and at 3.858Å from the centroid of its symmetry equivalent (symmetry operator for both centroids: $x, y-1, z$)

Experimental

A mixture of 2-chloronicotinic acid (1.57 g, 10 mmol) and thiophenol (2 ml) was heated under reflux for two hours to produce 2-(phenylsulfanyl) pyridine-3-carboxylic acid (Mann & Reid, 1952). The polyphosphoric acid (PPA) (Hidetoshi, 1997) was used to obtain 5*H*-benzothiopyrano[2,3-*b*]pyridin-5-one after cyclization. Crystals suitable for X-ray diffraction were obtained by cooling the saturated solution of the title compound in chloroform.

Refinement

For the molecule is disordered, during refinement EXYZ and EADP were used for N1A, C3B and N1B, C3A. The occupancy factors for N1A and N1B refined to 0.231 (4) and 0.269 (4), respectively. Thus, they were fixed to 0.25 whereas for C3A and C3B the site occupation factors were fixed to 0.75.

The H atoms were positioned geometrically, with C—H = 0.93 Å, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and constrained to ride on their parent atoms.

Figures

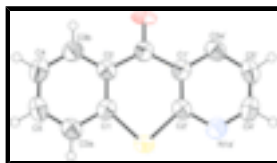


Fig. 1. ORTEP-3 for Windows (Farrugia, 1997) drawing of the title compound. The symmetry related atoms are shown by putting ' on the names. The displacement ellipsoids are drawn at the 50% probability level. H-atoms are shown by small circles of arbitrary radii.

5*H*-1-Benzothiopyrano[2,3-*b*]pyridin-5-one

Crystal data

C₁₂H₇NOS

$F_{000} = 220$

supplementary materials

$M_r = 213.26$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.7308$ (18) Å

$b = 3.8585$ (9) Å

$c = 15.771$ (3) Å

$\beta = 99.333$ (9)°

$V = 464.20$ (18) Å³

$Z = 2$

$D_x = 1.525$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1189 reflections

$\theta = 2.6$ – 28.7 °

$\mu = 0.31$ mm⁻¹

$T = 296$ (2) K

Needle, light yellow

$0.25 \times 0.06 \times 0.04$ mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 7.5 pixels mm⁻¹

$T = 296$ (2) K

ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2005)

$T_{\min} = 0.977$, $T_{\max} = 0.987$

5384 measured reflections

1189 independent reflections

822 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\text{max}} = 28.7$ °

$\theta_{\text{min}} = 2.6$ °

$h = -10 \rightarrow 10$

$k = -5 \rightarrow 3$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.070$

$wR(F^2) = 0.179$

$S = 1.17$

1189 reflections

83 parameters

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.435P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.62$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -

factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C6	0.3852 (15)	0.001 (3)	0.0576 (7)	0.044 (2)	0.50
O1	0.2856 (9)	-0.006 (2)	0.1093 (4)	0.083 (3)	0.50
C3B	0.1527 (4)	-0.2668 (8)	-0.05322 (19)	0.0508 (7)	0.75
H3B	0.0739	-0.2649	-0.0145	0.061*	0.75
N1B	0.3839 (4)	-0.2689 (8)	-0.17028 (19)	0.0530 (8)	0.25
S1	0.6613 (4)	-0.0009 (10)	-0.08029 (19)	0.0481 (6)	0.50
C3A	0.3839 (4)	-0.2689 (8)	-0.17028 (19)	0.0530 (8)	0.75
H3A	0.4605	-0.2676	-0.2100	0.064*	0.75
N1A	0.1527 (4)	-0.2668 (8)	-0.05322 (19)	0.0508 (7)	0.25
C1	0.4368 (4)	-0.1412 (8)	-0.08724 (19)	0.0444 (7)	
C2	0.3204 (4)	-0.1406 (8)	-0.02885 (17)	0.0437 (7)	
C4	0.1027 (4)	-0.3937 (9)	-0.1335 (2)	0.0577 (9)	
H4	-0.0102	-0.4803	-0.1495	0.069*	
C5	0.2178 (5)	-0.3955 (9)	-0.1919 (2)	0.0570 (9)	
H5	0.1816	-0.4842	-0.2467	0.068*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C6	0.045 (6)	0.038 (3)	0.047 (6)	0.002 (4)	0.002 (3)	0.008 (4)
O1	0.073 (4)	0.134 (6)	0.053 (4)	-0.023 (4)	0.047 (3)	-0.015 (4)
C3B	0.0496 (16)	0.0468 (16)	0.0563 (17)	-0.0002 (13)	0.0099 (13)	0.0016 (13)
N1B	0.0632 (19)	0.0482 (17)	0.0476 (15)	0.0023 (14)	0.0090 (13)	-0.0010 (13)
S1	0.0438 (17)	0.0620 (11)	0.0411 (16)	-0.0040 (13)	0.0145 (8)	-0.0032 (13)
C3A	0.0632 (19)	0.0482 (17)	0.0476 (15)	0.0023 (14)	0.0090 (13)	-0.0010 (13)
N1A	0.0496 (16)	0.0468 (16)	0.0563 (17)	-0.0002 (13)	0.0099 (13)	0.0016 (13)
C1	0.0434 (14)	0.0371 (14)	0.0512 (16)	0.0028 (12)	0.0031 (12)	0.0058 (12)
C2	0.0522 (16)	0.0361 (14)	0.0420 (14)	0.0059 (12)	0.0049 (12)	0.0037 (11)
C4	0.0501 (18)	0.0507 (19)	0.066 (2)	-0.0058 (14)	-0.0082 (15)	0.0034 (15)
C5	0.069 (2)	0.0495 (18)	0.0474 (17)	0.0000 (16)	-0.0075 (15)	-0.0048 (14)

Geometric parameters (\AA , $^\circ$)

C6—O1	1.209 (9)	S1—C2 ⁱ	1.791 (4)
C6—C2	1.480 (13)	S1—C1	1.803 (4)
C6—C1 ⁱ	1.481 (13)	C1—C2	1.388 (4)
C3B—C4	1.355 (4)	C1—C6 ⁱ	1.481 (13)
C3B—C2	1.380 (4)	C2—S1 ⁱ	1.791 (4)
C3B—H3B	0.9300	C4—C5	1.380 (5)
N1B—C5	1.364 (5)	C4—H4	0.9300
N1B—C1	1.398 (4)	C5—H5	0.9300

supplementary materials

O1—C6—C2	117.2 (11)	C6 ⁱ —C1—S1	15.5 (4)
O1—C6—C1 ⁱ	117.1 (11)	C3B—C2—C1	119.7 (3)
C2—C6—C1 ⁱ	125.7 (7)	C3B—C2—C6	123.3 (5)
C4—C3B—C2	120.0 (3)	C1—C2—C6	117.0 (5)
C4—C3B—H3B	120.0	C3B—C2—S1 ⁱ	107.4 (2)
C2—C3B—H3B	120.0	C1—C2—S1 ⁱ	132.9 (3)
C5—N1B—C1	118.7 (3)	C6—C2—S1 ⁱ	15.9 (4)
C2 ⁱ —S1—C1	94.30 (18)	C3B—C4—C5	120.6 (3)
C2—C1—N1B	120.0 (3)	C3B—C4—H4	119.7
C2—C1—C6 ⁱ	117.3 (5)	C5—C4—H4	119.7
N1B—C1—C6 ⁱ	122.7 (5)	N1B—C5—C4	120.9 (3)
C2—C1—S1	132.8 (3)	N1B—C5—H5	119.6
N1B—C1—S1	107.2 (2)	C4—C5—H5	119.6
C5—N1B—C1—C2	-0.8 (5)	S1—C1—C2—C6	0.2 (6)
C5—N1B—C1—C6 ⁱ	179.5 (6)	N1B—C1—C2—S1 ⁱ	-179.5 (3)
C5—N1B—C1—S1	179.4 (3)	C6 ⁱ —C1—C2—S1 ⁱ	0.2 (6)
C2 ⁱ —S1—C1—C2	-0.2 (4)	S1—C1—C2—S1 ⁱ	0.2 (6)
C2 ⁱ —S1—C1—N1B	179.6 (2)	O1—C6—C2—C3B	2.2 (15)
C2 ⁱ —S1—C1—C6 ⁱ	0(2)	C1 ⁱ —C6—C2—C3B	-179.7 (7)
C4—C3B—C2—C1	0.6 (5)	O1—C6—C2—C1	-178.2 (10)
C4—C3B—C2—C6	-179.8 (6)	C1 ⁱ —C6—C2—C1	-0.1 (12)
C4—C3B—C2—S1 ⁱ	-179.7 (3)	O1—C6—C2—S1 ⁱ	2.0 (11)
N1B—C1—C2—C3B	0.1 (4)	C1 ⁱ —C6—C2—S1 ⁱ	-180 (3)
C6 ⁱ —C1—C2—C3B	179.7 (6)	C2—C3B—C4—C5	-0.5 (5)
S1—C1—C2—C3B	179.8 (3)	C1—N1B—C5—C4	0.9 (5)
N1B—C1—C2—C6	-179.6 (6)	C3B—C4—C5—N1B	-0.2 (5)
C6 ⁱ —C1—C2—C6	0.1 (11)		

Symmetry codes: (i) $-x+1, -y, -z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5—H5 \cdots O1 ⁱⁱ	0.93	2.53	3.286 (7)	139

Symmetry codes: (ii) $x, -y-1/2, z-1/2$.

Fig. 1

