6-Hydroxy-s-triazolo[4,3-b]pyridazine: X-ray Analyses at 90 and 293 K

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$C_5H_4N_4O$, $M_r = 136\cdot1$, orthorhombic, space group $Fdd2$, $Z = 16$. At 90 (2) K: $a = 29\cdot097$ (8), $b = 21\cdot677$ (6), $c = 3\cdot618$ (1) Å, $V = 2282\cdot0$ Å^3, $D_x = 1\cdot584$ g cm^{-3}. At 293 (1) K: $a = 29\cdot112$ (9), $b = 21\cdot636$ (7), $c = 3\cdot701$ (1) Å, $V = 2331\cdot1$ Å^3, $D_m = 1\cdot55$ (2) (flotation), $D_x = 1\cdot551$ g cm^{-3}. The structures at 90 and 293 K are nearly identical; differences in the structural parameters are only those expected from changes of temperature. The title compound exists in the 'hydroxy' form. Planar molecules are linked by O(1)–H(1)···N(1) hydrogen bonds [2·589 (3) Å at 90 K; 2·606 (3) Å at 293 K] to make infinite ribbons parallel to *bc* diagonals. The parallel sets of ribbons are stacked together by van der Waals forces.

Introduction

6-Hydroxy-s-triazolo[4,3-b]pyridazine (hereinafter HTP) and its derivatives are reported to exist in the solid state in the lactam form (I*b*). This conclusion is based on the carbonyl absorption bands which appear in the region 1620–1640 cm^{-1}. All 'hydroxy' s-triazolo[4,3-b]pyridazines exhibit two broad bands in the region between 2600 and 1700 cm^{-1} due to strong hydrogen bonding (Tišler & Stanovnik, 1973; Linholter & Rosenoern, 1962). Recently, it has been demonstrated by ^{13}C NMR spectroscopy that neutral 'hydroxy' s-triazolo[4,3-b]pyridazines exist predominantly in the 'hydroxy' form in solution (I*a*) (Pugmire, Smith, Grant, Stanovnik, Tišler & Polanc, 1977). Because of these structural ambiguities it seemed worthwhile to reinvestigate the structure of this type of compound in the solid state.

(Ia)   (Ib)
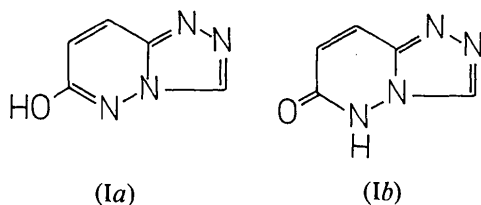
HTP crystallizes from dimethylformamide as transparent needles elongated along **c**. The systematically absent reflexions on Weissenberg photographs and the acentric distribution of |E| values at room temperature ($\langle E^2 \rangle = 1\cdot000$; $\langle |E^2 - 1| \rangle = 0\cdot817$; $\langle |E| \rangle = 0\cdot854$) indicate space group $Fdd2$ (No. 43). Unit-cell dimensions at 90 and 293 K were obtained from a least-squares fit of the 2θ values of 25 high-order reflexions measured on a CAD-4 diffractometer [Cu $K\alpha_1$ radiation, $\lambda = 1\cdot54051$ Å]. A single crystal with

approximate dimensions $0\cdot12 \times 0\cdot32 \times 0\cdot80$ mm was used for data collection on an automatic computer-controlled Enraf–Nonius CAD-4 four-circle diffractometer equipped with an Enraf–Nonius low-temperature device. Reflexions were scanned in the ω–2θ mode (moving crystal–moving counter) with a variable scan rate. For the measurements at 90 K a crystal with dimensions $0\cdot10 \times 0\cdot21 \times 0\cdot65$ mm was cooled in a stream of cold nitrogen gas. The largest contraction on cooling is observed in the **c** axis direction and there is no phase transition in this temperature range. Details of data collection and reduction are given in Table 1. The data were corrected

Table 1. *Data-collection summary for HTP*

Diffractometer	CAD-4 automatic, four-circle	
Radiation	Cu $K\bar{\alpha}$ (Ni-filtered) ($\bar{\lambda} = 1\cdot5418$ Å)	
Scan method	ω–2θ	
2θ scan width (°)	$0\cdot9 + 0\cdot2$ tan θ	
Scan rate [(°) min^{-1}]	Min: $2\cdot0$; max: $20\cdot1$	
Background	$\frac{1}{4}$ of the scan time at each of the scan limits	
$2\theta_{max}$ (°)	150	
Maximum scan time (s)	40	
Aperture (mm)	$2\cdot5 + 0\cdot9$ tan θ	
Reference reflexions	331, $\bar{1}31$, $\bar{2}22$	
$\sigma(I)$ based on	Counting statistics	
	90 K	**293 K**
Measured reflexions	1460	3833
	($\pm h$,$+k$,$+l$)	($\pm h$,$\pm k$,$+l$)
Averaged reflexions	688	727
Mean discrepancy on I (%)	3·9 (for 1370 reflexions)	9·0 (for 3649 reflexions)
Observed reflexions	623	659
Unobserved reflexions [$I < 3\cdot0 \times \sigma(I)$]	65	68
Linear absorption coefficient (cm^{-1}) for Cu $K\bar{\alpha}$	10·28	10·07

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'or variation in reference reflexions and Lorentz–polarization effects. No absorption corrections have been made.

The structure was solved by direct methods with *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974) from the room-temperature data, which were available first. An E map with the highest combined figure of merit CFOM (3·000) obtained with the unit weighting of ABSFOM (1·078), ψ_0 (398) and RESID (41·72), computed with 250 phases ($|E| >$ 1·00), gave initial coordinates for all the heavy atoms. The structure refinements of both sets of X-ray data were by full-matrix least squares, minimizing the function $\Sigma\, w(F_o - kF_c)^2$, where the weighting function was determined empirically:

$$w = w_F\, w_S,$$

where

$$w_F(|F_o| < A) = (|F_o|/A)^C,$$

$$w_F(|F_o| > B) = (B/|F_o|)^P,$$

$$w_F(A < |F_o| < B) = 1\cdot 0$$

and

$$w_S(\sin\theta < G) = (\sin\theta/G)^J,$$

$$w_S(\sin\theta > H) = (H/\sin\theta)^K,$$

$$w_S(G < \sin\theta < H) = 1\cdot 0.$$

Anisotropic temperature factors were adopted for the nonhydrogen atoms. Difference Fourier syntheses revealed all the H atoms at the expected positions. They were included in the refinement with isotropic tem-

Table 2. *Refinement summary*

	90 K	293 K
Final refinement cycle		
Scale factor (k)	0·491	0·759
$R = \Sigma\,|\Delta F|/\Sigma\,|F_o|$	0·049	0·047
$R_w = [\Sigma\, w(\Delta F)^2/\Sigma\, wF_o^2]^{1/2}$	0·050	0·047
Average shift/error	0·006	0·011
Maximum shift/error	0·057	0·066
Data(m)-to-variable(n) ratio	6·5	6·8
$[\Sigma\, w(\Delta F)^2/(m - n)]^{1/2}$	0·775	0·899
Final difference map		
Maximum $\Delta\rho$ (e Å^{-3})	0·16	0·23
Weighting-function parameters		
A	20·00	13·00
B	58·00	64·00
C	1·00	1·00
D	4·00	3·00
G	0·60	0·60
H	0·92	0·92
J	4·00	4·00
K	1·00	1·00

Table 3. *Final fractional coordinates and thermal parameters with standard deviations in parentheses*

Coordinates are multiplied by 10^4 for nonhydrogen and by 10^3 for hydrogen atoms. The anisotropic and isotropic temperature factors (Å^2) are expressed in the form $\exp\{-2\pi^2[U(11)h^2a^{*2} + 2U(12)hka^*b^* + ...] \times 10^{-4}\}$ and $\exp[-8\pi^2 U(\sin\theta/\lambda)^2 \times 10^{-3}]$ respectively. Upper numbers: 90 K, lower numbers: 293 K.

	x	y	z	$U(11)$	$U(22)$	$U(33)$	$U(12)$	$U(13)$	$U(23)$
O(1)	2947 (1)	7939 (1)	7526 (11)	165 (9)	114 (9)	402 (14)	10 (7)	6 (10)	−72 (9)
	2954 (1)	7931 (1)	7571 (12)	311 (9)	416 (11)	723 (17)	2 (8)	3 (11)	−217 (12)
N(1)	4306 (1)	6484 (1)	2868	169 (11)	104 (10)	307 (15)	−25 (9)	29 (13)	−20 (10)
	4302 (1)	6486 (1)	2868	328 (10)	348 (11)	495 (17)	−29 (9)	49 (14)	−115 (12)
N(2)	4660 (1)	6885 (1)	3673 (13)	189 (11)	99 (10)	352 (16)	−28 (9)	7 (12)	−13 (12)
	4653 (1)	6886 (1)	3647 (13)	310 (10)	440 (12)	554 (18)	−58 (10)	55 (12)	−99 (14)
C(3)	4478 (1)	7389 (1)	5070 (14)	176 (12)	92 (11)	329 (16)	−7 (10)	−6 (15)	0 (12)
	4476 (1)	7381 (1)	5023 (14)	306 (12)	365 (13)	525 (18)	−64 (11)	−30 (15)	−55 (14)
N(4)	4011 (1)	7327 (1)	5216 (12)	157 (10)	53 (9)	270 (13)	2 (8)	−2 (11)	5 (10)
	4012 (1)	7324 (1)	5217 (12)	270 (9)	310 (10)	381 (13)	−17 (8)	6 (10)	−45 (11)
N(5)	3705 (1)	7758 (1)	6545 (12)	168 (11)	83 (9)	289 (15)	13 (8)	0 (12)	−19 (10)
	3706 (1)	7750 (1)	6556 (12)	312 (10)	321 (10)	413 (15)	−7 (8)	−14 (11)	−96 (11)
C(6)	3275 (1)	7569 (1)	6314 (14)	176 (13)	117 (11)	268 (15)	3 (10)	−8 (13)	−26 (12)
	3279 (1)	7565 (1)	6342 (14)	305 (12)	355 (12)	430 (16)	24 (10)	−12 (13)	−70 (13)
C(7)	3131 (1)	6980 (1)	4858 (13)	173 (13)	101 (12)	329 (17)	−23 (9)	4 (14)	−9 (12)
	3135 (1)	6975 (1)	4916 (14)	284 (12)	420 (14)	549 (19)	−69 (10)	17 (14)	−123 (15)
C(8)	3446 (1)	6569 (1)	3643 (13)	179 (12)	106 (11)	281 (15)	−27 (9)	1 (12)	−25 (13)
	3447 (1)	6569 (1)	3697 (13)	347 (12)	327 (12)	454 (17)	−86 (10)	15 (12)	−108 (14)
C(9)	3916 (1)	6755 (1)	3854 (13)	190 (13)	80 (10)	239 (15)	−10 (9)	16 (12)	1 (13)
	3916 (1)	6757 (1)	3862 (12)	319 (12)	317 (11)	380 (15)	−37 (10)	40 (12)	−28 (14)
H(1)	303 (2)	836 (3)	830 (18)	42 (12)					
	305 (2)	826 (2)	789 (17)	58 (12)					
H(3)	463 (2)	777 (2)	593 (17)	35 (11)					
	462 (2)	773 (2)	586 (13)	43 (9)					
H(7)	282 (2)	692 (2)	487 (16)	34 (12)					
	282 (1)	690 (2)	525 (12)	33 (9)					
H(8)	336 (1)	612 (2)	274 (11)	12 (7)					
	338 (1)	617 (2)	288 (10)	22 (7)					

perature factors. The final difference electron-density maps were featureless. Final refinement parameters together with the weighting-function parameters are given in Table 2. Atomic scattering factors for H were those of Stewart, Davidson & Simpson (1965) and for other atoms were those of Cromer & Mann (1968). All calculations were carried out on the CDC Cyber 72 computer at RRC Ljubljana. The XRAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used during the refinement and the final interpretation of the results.

In Table 3 the final atomic coordinates and thermal parameters of HTP at 90 and 293 K are listed.*

Discussion

Fig. 1 shows a molecule of HTP at 90 and 293 K together with the values of the interatomic bond

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* Structure factors for HTP at 90 and 293 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32693 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

distances. Interatomic distances and angles with estimated standard deviations are given in Table 4. Fig. 2 provides a stereoscopic view of the molecular packing.

Table 3 shows that there are no essential differences between the structures at 90 and 293 K. The corrections for bond shortening due to thermal vibrations, applied on the basis of the rigid-body TLS analysis [Schomaker & Trueblood (1968); computer program written by Filippini & Gramaccioli (1969)] to the two sets of data, are equal to or smaller than the standard deviations of the atomic coordinates. However, the orientation of the thermal ellipsoids is different at different temperatures. These effects are presumably due to the short intermolecular hydrogen bond O(1)—H(1)···N(1), which links the molecules into infinite ribbons parallel to [011] and prevents the librational motion of the molecules.

Apart from a comparison of the bond lengths and angles (Table 4), only the low-temperature structure
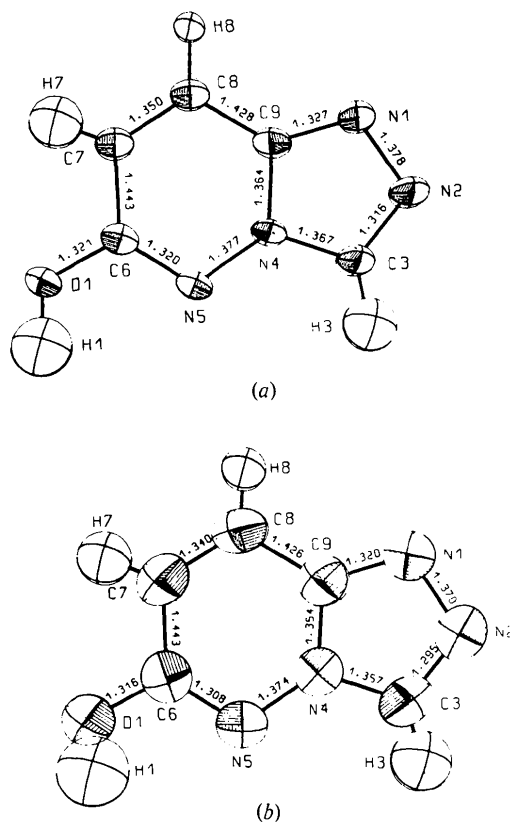

Fig. 1. The molecule at (a) 90 K and (b) 293 K viewed along the normal to the mean plane. The atoms are represented by thermal ellipsoids drawn at the 80% probability level (Johnson, 1965).

Table 4. *Bond distances* (Å) *and bond angles* (°)

|	90 K	293 K
O(1)—C(6)	1·321 (4)	1·316 (4)
N(1)—N(2)	1·378 (3)	1·370 (3)
N(1)—C(9)	1·327 (4)	1·320 (4)
N(2)—C(3)	1·316 (4)	1·295 (5)
C(3)—N(4)	1·367 (4)	1·357 (3)
N(4)—N(5)	1·377 (4)	1·374 (4)
N(4)—C(9)	1·364 (4)	1·354 (4)
N(5)—C(6)	1·320 (4)	1·308 (3)
C(6)—C(7)	1·443 (4)	1·443 (5)
C(7)—C(8)	1·350 (4)	1·340 (4)
C(8)—C(9)	1·428 (4)	1·426 (4)
C(3)—H(3)	0·99 (5)	0·92 (4)
C(7)—H(7)	0·93 (5)	0·94 (4)
C(8)—H(8)	1·05 (4)	0·94 (3)
N(2)—N(1)—C(9)	107·7 (2)	107·3 (2)
N(1)—N(2)—C(3)	107·7 (2)	107·8 (2)
N(2)—C(3)—N(4)	109·5 (3)	110·0 (3)
C(3)—N(4)—N(5)	126·1 (3)	127·1 (3)
C(3)—N(4)—C(9)	106·1 (2)	105·6 (3)
N(5)—N(4)—C(9)	127·8 (2)	127·3 (2)
N(4)—N(5)—C(6)	112·3 (2)	112·9 (3)
O(1)—C(6)—N(5)	118·3 (3)	118·6 (3)
O(1)—C(6)—C(7)	116·7 (3)	116·7 (2)
N(5)—C(6)—C(7)	124·9 (3)	124·6 (3)
C(6)—C(7)—C(8)	120·4 (3)	120·4 (3)
C(7)—C(8)—C(9)	116·5 (3)	116·5 (3)
N(1)—C(9)—N(4)	109·0 (2)	109·2 (2)
N(1)—C(9)—C(8)	133·0 (3)	132·6 (3)
N(4)—C(9)—C(8)	118·0 (3)	118·2 (3)
O(1)—H(1)	0·99 (6)	0·78 (6)
N(1)···H(1)	1·62 (6)	1·86 (6)
O(1)···N(1)	2·589 (3)	2·606 (4)
C(6)—O(1)···N(1)	117·6 (2)	117·9 (2)
O(1)—H(1)···N(1)	168 (5)	159 (5)
C(6)··O(1) H(1)	119 (3)	111 (4)
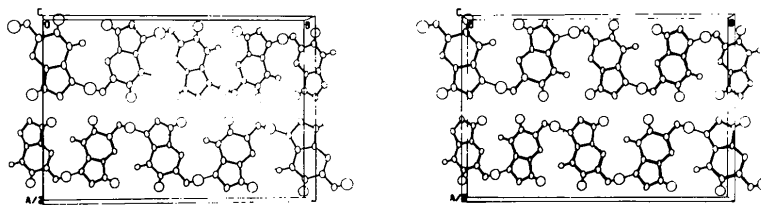
Fig. 2. A stereoscopic view of the two 'ribbons' of molecules as seen down [001].

will be discussed. Most of the bond lengths and angles are within normal ranges. The somewhat shorter C(3)—N(2) [1·316 (4)], C(9)—N(1) [1·327 (4)], C(7)—C(8) [1·350 (4)] and C(6)—N(5) [1·320 (4) Å] bonds demonstrate double-bond character, whereas the remaining bonds have single-bond character. The molecule exists in the enol form, H(1) being attached to O(1).

The molecule is planar, described by the equation $0·0734X - 0·3947Y + 0·9159Z = -3·6782$ Å, where X, Y and Z refer to the a, b and c axes. The largest deviations from the least-squares plane are −0·010, 0·014 and −0·014 Å for O(1), C(7) and C(9) respectively. The angle (0·6°) between the pyridazine and s-triazole part of HTP is not significantly different from zero.

The molecules are interconnected by a rather strong hydrogen bond, O(1)—H(1)···N(1) [2·589 (3) Å at 90K; 2·606 (3) Å at 293 K], to form infinite ribbons along the bc diagonal (Fig. 2). The ribbons follow alternate diagonals parallel to the bc plane; parallel sets of ribbons are separated by 3·315 Å, a value somewhat smaller than the c parameter of the unit cell (3·701 Å). All contacts between the ribbons correspond to normal van der Waals distances.

References

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.

FILIPPINI, G. & GRAMACCIOLI, C. M. (1969). *Ric. Sci.* 39, 156–162.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

LINHOLTER, S. & ROSENOERN, R. (1962). *Acta Chem. Scand.* 16, 2389–2394.

MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN 74, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain-la-Neuve, Belgium.

PUGMIRE, R. J., SMITH, J. C., GRANT, D. M., STANOVNIK, B., TIŠLER, M. & POLANC, S. (1977). *J. Heterocycl. Chem.* 14. In the press.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B24, 63–76.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

TIŠLER, M. & STANOVNIK, B. (1973). *Azolo- and Azinopyridazines and Some Oxa and Thia Analogs* in *Condensed Pyridazines Including Cinnolines and Phthalazines,* pp. 761–1056. New York: Wiley–Interscience.