

Crystal Structure of 8-Methyl-dihydrothiazolo[3,2-*a*]pyridin-5-one Trihydrate at -160°C

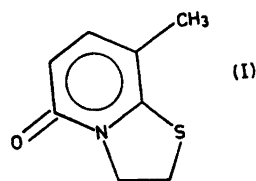
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The crystals are orthorhombic with space group $Pbca$. There are eight formula units in the cell with dimensions $a=6.926(2)$ Å, $b=14.172(2)$ Å, $c=21.308(6)$ Å. The structure was solved by direct methods and refined by full-matrix least-squares technique to $R=3.3\%$ ($R_w=3.5\%$) for 1367 observed reflections (automatic four circle diffractometer). The crystal structure is built up of ribbons of water molecules (parallel to the bc -plane) to pairs of which the pyridinone molecules are attached at both sides by hydrogen bonds of length 2.789 and 2.749 Å. Between the layers thus formed van der Waals' forces only reside.

Rearrangement studies in dihydrothiazolo[3,2-*a*]pyridinium salts¹ have yielded a pyridinone,

* All programs used (except those for phase determination and stereoscopic drawing) are included in this reference.



viz. 8 methyl-dihydrothiazolo[3,2-*a*]pyridin-5-one (I) which is characterized by an unexpectedly low melting point. In order to explore the reason for this, an X-ray crystallographic investigation has been carried out.

The crystals of $\text{C}_7\text{H}_9\text{SON}\cdot 3\text{H}_2\text{O}$ are orthorhombic with cell dimensions $a=6.926(2)$ Å, $b=14.172(2)$ Å, $c=21.308(6)$ Å. The space group is $Pbca$ and there are eight formula units in the unit cell ($D_m=1.38$ g cm^{-3} , $D_x=1.40$ g cm^{-3}). Since the compound has a melting

Table 1. Final fractional coordinates and thermal parameters with estimated standard deviations. Expression for anisotropic vibration is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})]$. Hm and Hm_n are bonded to Cm. HWm_n is bonded to OWm.

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
S	.6699(3)	.4598(4)	.5988(10)	.0154(3)	.0084(3)	.0238(3)	-.0009(2)	.0016(3)	-.0002(3)
O	.5821(4)	.1463(11)	.6871(26)	.0151(9)	.0158(9)	.0242(9)	-.0028(7)	-.0007(8)	.0029(7)
N	.6327(9)	.2662(13)	.6449(27)	.0126(11)	.0110(9)	.0161(11)	.0005(7)	-.0013(8)	.0001(8)
C1	.6850(18)	.3387(18)	.6813(35)	.0177(12)	.0105(11)	.0187(12)	.0017(9)	.0014(11)	.0004(10)
C2	.5937(12)	.4413(16)	.7187(38)	.0198(14)	.0128(12)	.0233(15)	.0016(10)	.0034(12)	.0007(11)
C3	.5748(11)	.3486(15)	.6785(48)	.0142(13)	.0148(12)	.0199(13)	.0038(10)	.0023(12)	.0002(11)
C4	.6327(11)	.1886(15)	.6487(33)	.0207(14)	.0105(12)	.0115(13)	-.0006(9)	.0048(10)	.0005(10)
C5	.6917(11)	.1459(16)	.6874(37)	.0219(13)	.0096(12)	.0155(13)	.0026(9)	-.0013(11)	.0001(10)
C6	.7431(12)	.1985(17)	.5646(34)	.0143(13)	.0201(14)	.0168(13)	.0047(10)	-.0013(11)	-.0009(11)
C7	.7416(11)	.2979(17)	.5619(32)	.0152(13)	.0169(13)	.0151(13)	.0001(10)	-.0004(11)	.0014(10)
C8	.7987(13)	.3563(20)	.5217(48)	.0166(14)	.0222(15)	.0328(17)	.0025(11)	.0010(13)	.0047(13)
OW1	.4423(9)	.0465(14)	.2030(29)	.0304(11)	.0158(10)	.0208(12)	.0042(8)	-.0068(9)	.0024(9)
OW2	.9873(9)	.3374(12)	.4877(30)	.0179(10)	.0205(10)	.0265(11)	-.0005(8)	.0037(9)	.0016(9)
OW3	.9891(9)	.1617(14)	.5299(32)	.0206(11)	.0167(10)	.0279(12)	-.0033(8)	.0006(9)	.0004(9)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H21	.8661(11)	.4859(17)	.6586(36)	1.2(5)	H22	.6804(11)	.4511(16)	.8565(38)	1.4(5)
H31	.5516(11)	.3393(16)	.5457(39)	1.4(5)	H32	.5492(10)	.3158(15)	.7782(35)	.9(4)
H5	.6932(11)	.0603(18)	.6139(38)	1.7(5)	H6	.7816(12)	.1787(18)	.5356(35)	1.2(5)
H81	.7891(13)	.4193(20)	.4387(41)	2.6(8)	H82	.8292(15)	.3282(22)	.4853(48)	4.1(8)
H83	.8172(12)	.3779(18)	.6324(43)	2.2(8)	HW11	.4285(14)	-.0058(22)	.2924(46)	3.4(8)
HW12	.4384(13)	.0731(20)	.1868(44)	2.2(7)	HW21	.9919(14)	.3482(18)	.3888(42)	2.8(7)
HW22	.9511(13)	.3742(20)	.5861(46)	2.6(7)	HW31	.9286(14)	.1582(21)	.6539(52)	3.3(7)
HW32	.9226(14)	.2864(21)	.4913(43)	2.1(7)					

Table 2. Bond distances and angles with estimated standard deviation.

DISTANCE	(Å)	DISTANCE	(Å)
S - C1	1,749(2)	S - C2	1,826(2)
N - C1	1,372(3)	N - C3	1,482(3)
C2 - C3	1,818(3)	N - C4	1,383(3)
O - C4	1,282(3)	C4 - C5	1,413(3)
C5 - C6	1,371(3)	C6 - C7	1,498(3)
C7 - C1	1,366(3)	C7 - C8	1,498(3)

ANGLE	(°)	ANGLE	(°)
C1 - S - C2	91,4(1)	S - C2 - C3	106,6(2)
C2 - C3 - N	106,4(2)	C3 - N - C1	115,3(2)
N - C1 - S	112,2(2)	C3 - N - C4	121,3(2)
N - C4 - O	118,7(2)	O - C4 - C5	125,1(2)
N - C4 - C5	119,2(2)	C4 - C5 - C6	121,3(2)
C5 - C6 - C7	122,1(2)	C6 - C7 - C1	116,2(2)
C6 - C7 - C8	122,8(2)	C6 - C7 - C1	121,3(2)
C7 - C1 - N	122,0(2)	C7 - C1 - S	125,7(2)

DISTANCE	(Å)	DISTANCE	(Å)
O - OH1'	2,789(2)	O - OH2'	2,749(3)
OH1 - OH2'	2,719(3)	OH1 - OH3'	2,798(3)
OH2 - OH3'	2,826(3)	OH2 - OH3'	2,817(3)
OH1 - NH11	,798(31)	OH1 - NH12	,887(38)
OH2 - NH21	,761(31)	OH2 - NH22	,867(32)
OH3 - NH31	,988(36)	OH3 - NH32	,746(38)

ANGLE	(°)	ANGLE	(°)
O - NH11' - OH1'	165(3)	O - NH21' - OH2'	177(3)
OH1 - NH22' - OH2'	177(3)	OH1 - NH12' - OH3'	169(3)
OH2 - NH32' - OH3'	175(3)	OH2 - NH31' - OH3'	178(3)

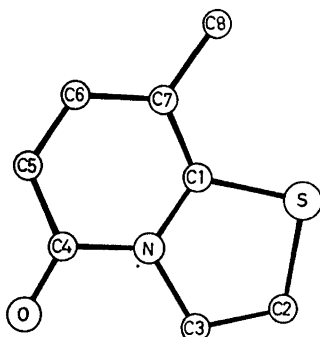


Fig. 1. Schematic drawing of the pyridinone molecule.

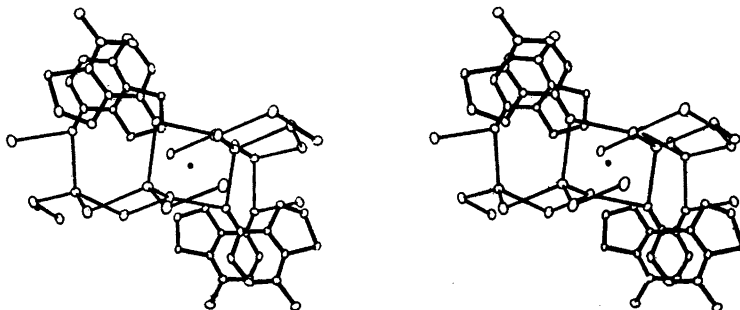


Fig. 2. Stereoscopic view (approximately along [001]) showing the hydrogen bonding network (b-axis across the page).

point of about 28 °C the intensities were measured at -160 °C (on a Syntex PI diffractometer with an Enraf-Nonius liquid nitrogen cooling device modified by H. Hope). The radiation was $MoK\alpha$ ($\lambda = 0.71069 \text{ \AA}$) and $2\theta_{\max} = 50^\circ$. With an observed-unobserved cutoff at $2.5 \sigma(I)$, 1367 reflections were recorded as observed. The crystal size was $(0.2 \times 0.3 \times 0.35) \text{ mm}^3$. No corrections were made for absorption or secondary extinction effects.

The structure was solved by direct methods² and refined by full-matrix least-squares technique.^{3,*} Anisotropic temperature factors were introduced for the heavy atoms. All hydrogen atoms were localized in the difference Fourier map. Atomic form factors were those of Hanson *et al.*⁴ except for hydrogen.⁵ Weights used in least-squares were obtained from the standard deviations in intensities, $\sigma(I)$, taken as

$$\sigma(I) = [C_T + (0.02 C_N)^2]^{1/2}$$

where C_T is the total number of counts and C_N the net count. The final R -value was 3.3 % ($R_w = 3.4 \%$) for 1367 observed reflections.

Final fractional coordinates and thermal parameters with estimated standard deviations are given in Table 1. The principal axes of the thermal vibration ellipsoids were calculated from the temperature parameters of Table 1. Maximum r.m.s. amplitudes range from 0.129 to 0.193 Å (corresponding B -values of 1.31 and 2.94 Å²). No rigid-body analysis of translational, librational and screw motion has been carried out.

Bond distances and angles (including hydrogen bonds) are listed in Table 2. The standard deviations, given in parentheses, are estimated

from the correlation matrix of the final least-squares refinement cycle. Fig. 1 is a schematic drawing of the molecule.

The system S, O, N, C1, C3, ..., C8 is planar (to within 0.03 Å) with C2 0.42 Å out of the plane. This puckering of the five-membered ring (and the bond distances and angles as well) agree, within error limits, with the results obtained for *trans*-2-carboxy-5-methyl-dihydrothiazolo[3,2-*a*]pyridinium-3-carboxylate⁶ and *cis*-2,3-(3'-cyclohexanone-1',2'-ylene)-5-methyl-8-ethoxydihydrothiazolo[3,2-*a*]pyridinium bromide.⁷

The crystals contain as much as 24.4 % water (a fact which possibly may be held responsible for the low melting point). The water molecules form a rather complex network of hydrogen bonds. A fragment of this is shown in a stereoscopic drawing⁸ (Fig. 2) where the structure is viewed approximately along [001] (with the *b*-axis across the page) and a centre of symmetry is indicated. The fact that the carbonyl oxygen atom accepts two hydrogen bonds (from OW1 and OW2) is reflected in the C=O bond length of 1.262 Å. As may be seen from Table 2, OW1 and OW3 are involved in three, and OW2 in four hydrogen bonds. Inspection of Fig. 2 shows that O, OW1, and OW2 together with their centro-symmetrically related equivalents constitute chair-formed six-membered rings which are linked together by six water molecule (OW3) bridges. These bridges form condensed five-membered rings and the whole network may be characterized as ribbons of water molecules (parallel to the *bc*-plane) to pairs of which the pyridinone molecules are attached at both sides. Between the layers thus formed van der Waals forces only reside.

Acknowledgement. The author would like to thank cand. real. T. Lærum for preparing the crystals.

REFERENCES

1. Undheim, K. *Personal communication.*
2. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
3. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
4. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Crystallogr.* 17 (1964) 1040.
5. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
6. Groth, P. *Acta Chem. Scand.* 25 (1971) 118.
7. Groth, P. *Acta Chem. Scand.* 26 (1972) 3131.
8. Johnson, C. K. *ORTEP*, Report ORNL-3795, Oak Ridge National Laboratory, Oak Ridge 1965.

Received December 21, 1976.