

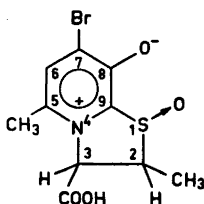
The Crystal Structure of 7-Bromo-3-carboxy-2,5-dimethyl-1-oxo-dihydrothiazolo[3,2-a]pyridinium-8-hydroxylate

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The crystal structure of 7-bromo-3-carboxy-2,5-dimethyl-1-oxo-dihydrothiazolo[3,2-a]pyridinium-8-hydroxylate, $C_{10}H_{10}BrNO_4S$, has been solved by X-ray crystallographic methods. The crystals are orthorhombic, space group *Pbca*, with 8 molecules in the unit cell. The cell dimensions are: $a = 11.66 \text{ \AA}$, $b = 12.75 \text{ \AA}$, $c = 15.48 \text{ \AA}$. The intensity data were collected by means of an automatic equi-inclination diffractometer. The structure was solved by the heavy atom method and refined by least-squares technique to an *R*-value of 0.050. Within a molecule, the sulfoxide group and the carboxyl group are on the same side of the plane of the pyridine ring whereas the 2-methyl group is on the opposite side of this plane. The molecules are linked together by strong hydrogen bonds.

This paper reports the three-dimensional crystal structure analysis of 7-bromo-3-carboxy-2,5-dimethyl-1-oxo-dihydrothiazolo[3,2-a]pyridinium-8-hydroxylate:



The preparation of this compound and the discussion of the chemical aspects are given in a separate paper by Undheim and Greibrokk¹ who provided suitable single crystals.

EXPERIMENTAL

Unit cell and space group. The dimensions of the orthorhombic unit cell, derived from precession photographs applying Zr-filtered Mo-radiation, are: $a = 11.66(2)$ Å, $b = 12.75(2)$ Å, and $c = 15.48(2)$ Å. The standard deviations, estimated from repeated measurements, are given in parenthesis. The space group was unequivocally established from the systematic extinctions as *Pbca* which has eight-fold general positions. The density found by flotation was 1.83 g cm^{-3} , in fair agreement with a calculated density of 1.85 g cm^{-3} assuming 8 molecules per unit cell.

Collection of intensity data. A nearly isodiametric (0.2 mm) crystal was mounted with the *a*-axis as rotation axis. The intensity measurements were performed by means of an automatic equi-inclination diffractometer (Stoe & Cie, Darmstadt, DBR). $\text{MoK}\alpha$ -radiation was selected using a LiF monochromator. Harmonics were excluded by using a scintillation detector with proper settings of a pulse height discriminator. The relative intensities of reflexions $0kl$ through $13kl$ ($\sin\theta_{\text{max}}/\lambda = 0.60$) were measured by ω -scanning. 775 reflexions having net intensities less than twice their standard deviation, calculated from counting statistics, were considered unobserved. This left a total of 1278 independent observations.

Computer programs. A FORTRAN program PAULUS 67 calculated setting angles for the diffractometer. Consistency of the diffractometer output data was checked by an ALGOL program PDR, which also calculates intensities and standard deviations. The FORTRAN program LP converted the intensities to relative structure factors by means of the conventional L_p correction formulas, ignoring the pre-polarization of the incident beam. No correction for absorption was made; μ for $\text{MoK}\alpha$ is 39.2 cm^{-1} . The calculations for the regular structure analysis were performed using the program system X-RAY 63.² All calculations were carried out on the IBM 7094 computer at NEUCC and on the GIER computer, both situated at the Technical University of Denmark, Lyngby.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The bromine atom was located from a three-dimensional Patterson map. The positions of the remaining non-hydrogen atoms were derived from successive Fourier syntheses. Atomic scattering factors were taken from *International Tables*.³ The parameters thus obtained were then refined by a full-matrix least squares procedure, using first isotropic temperature factors and later anisotropic temperature factors. The weighting function used was the one suggested by Killean *et al.*:⁴ $1/\sqrt{w} = \sqrt{\sigma_1^2(F_o) + \sigma_2^2(F_o)}$. In this expression, $\sigma_1(F_o)$ refers to the counting statistical error, and $\sigma_2(F_o)$ refers to the random setting error. $\sigma_2(F_o)$ is estimated as $c|F_o|$ where the value of the constant c is adjusted as described by Killean. This refinement terminated with residuals $R = 0.059$ and $R_w = 0.085$.

Now, a three-dimensional difference-Fourier synthesis was computed. In this Fourier map, all the hydrogen atoms could be located at reasonable positions, although some of the peaks were only slightly above the background fluctuations of electron density. The least squares procedure was then reassumed including the hydrogen atoms. Thermal movement of the hydrogen atoms was accounted for by fixed isotropic parameters $B = 3.5$. The constant c in the weighting function was assigned a value of 0.041 in the final refinement which terminated with residuals $R = 0.050$ and $R_w = 0.066$. The standard deviation of an observation of unit weight was 1.17.

The final positional and thermal parameters with their estimated standard deviations are given in Tables 1 and 2. A list of observed and calculated structure factors may be obtained from the author upon request.

Table 1. Positional parameters as fractions of cell edges with 10⁴ times their estimated standard deviations.

Atom	<i>x</i>	$\sigma(x)$	<i>y</i>	$\sigma(y)$	<i>z</i>	$\sigma(z)$
Br	0.3090	(1)	0.5500	(1)	0.0301	(1)
S	0.6847	(2)	0.4780	(2)	0.2538	(1)
N	0.5681	(5)	0.3347	(5)	0.1671	(4)
O1	0.7940	(4)	0.4878	(5)	0.2028	(4)
O2	0.5019	(4)	0.6105	(4)	0.1525	(4)
O3	0.7613	(5)	0.2496	(6)	0.0891	(4)
O4	0.8403	(5)	0.2113	(5)	0.2177	(4)
C2	0.6761	(7)	0.3451	(6)	0.2980	(5)
C3	0.6520	(7)	0.2749	(6)	0.2211	(5)
C5	0.4945	(7)	0.2910	(7)	0.1101	(5)
C6	0.4176	(6)	0.3571	(7)	0.0681	(6)
C7	0.4180	(6)	0.4635	(6)	0.0840	(5)
C8	0.4986	(5)	0.5125	(6)	0.1409	(5)
C9	0.5716	(6)	0.4401	(6)	0.1807	(5)
C10	0.5847	(10)	0.3454	(9)	0.3683	(6)
C11	0.7584	(7)	0.2445	(7)	0.1672	(6)
C12	0.4942	(9)	0.1734	(8)	0.0972	(6)
H1	0.8882	(87)	0.1606	(88)	0.1887	(66)
H2	0.7471	(94)	0.3344	(82)	0.3249	(71)
H3	0.6180	(86)	0.2066	(88)	0.2365	(70)
H4	0.3682	(92)	0.3201	(89)	0.0291	(67)
H5	0.5983	(85)	0.3876	(90)	0.4223	(75)
H6	0.6081	(92)	0.2858	(92)	0.4059	(70)
H7	0.5251	(93)	0.3388	(94)	0.3392	(70)
H8	0.4358	(88)	0.1613	(87)	0.0444	(66)
H9	0.5692	(96)	0.1461	(95)	0.0932	(68)
H10	0.4691	(103)	0.1481	(101)	0.1387	(71)

Table 2. Anisotropic temperature factor parameters with their estimated standard deviations in units of 10⁻⁴ Å².

Atom	<i>U</i> ₁₁ $\sigma(U_{11})$	<i>U</i> ₂₂ $\sigma(U_{22})$	<i>U</i> ₃₃ $\sigma(U_{33})$	<i>U</i> ₁₂ $\sigma(U_{12})$	<i>U</i> ₁₃ $\sigma(U_{13})$	<i>U</i> ₂₃ $\sigma(U_{23})$
Br	421 (4)	601 (6)	408 (5)	76 (4)	- 14 (4)	134 (5)
S	456 (10)	264 (10)	311 (11)	- 60 (9)	- 75 (9)	- 2 (9)
N	401 (29)	211 (35)	191 (34)	- 19 (28)	- 24 (26)	- 22 (28)
O1	489 (30)	563 (42)	549 (42)	- 132 (30)	- 25 (30)	152 (35)
O2	487 (29)	196 (35)	499 (38)	11 (25)	- 85 (29)	43 (29)
O3	581 (32)	652 (44)	308 (36)	225 (33)	69 (30)	58 (38)
O4	532 (32)	351 (35)	414 (37)	107 (26)	- 2 (28)	27 (29)
C2	533 (45)	229 (43)	284 (45)	22 (37)	- 104 (39)	33 (35)
C3	560 (42)	163 (45)	240 (43)	- 19 (33)	27 (36)	- 28 (34)
C5	522 (44)	309 (50)	256 (43)	- 129 (39)	76 (39)	- 52 (38)
C6	370 (37)	362 (55)	358 (50)	- 149 (37)	- 8 (36)	9 (43)
C7	290 (33)	371 (54)	279 (42)	23 (32)	87 (32)	99 (38)
C8	240 (30)	262 (45)	325 (43)	58 (29)	9 (31)	95 (38)
C9	365 (33)	200 (42)	282 (41)	- 43 (33)	- 37 (32)	- 33 (37)
C10	867 (72)	489 (64)	204 (52)	- 227 (61)	87 (49)	- 102 (48)
C11	440 (38)	254 (46)	374 (51)	38 (38)	- 28 (39)	52 (43)
C12	617 (54)	291 (54)	407 (62)	- 56 (44)	6 (49)	- 154 (47)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Fig. 1 shows a molecule of the structure as viewed along the a axis. Bond lengths and bond angles with their estimated standard deviations are given in Tables 3 and 4. As one would expect, all distances and angles involving the hydrogen atoms are associated with large errors.

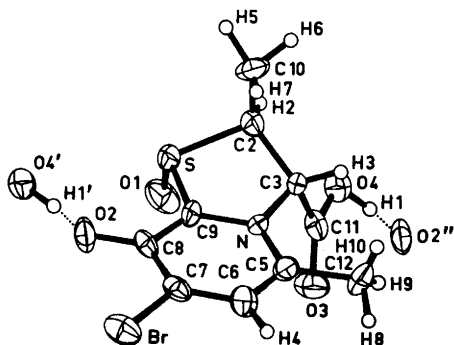


Fig. 1. The structure viewed along the a axis drawn by the program ORTEP.⁶ The thermal ellipsoids include 50 % of the electron density distribution.

Table 3. Interatomic distances in Å with 10^3 times their estimated standard deviations. Atoms designated with a prime belong to the neighbouring molecule ($3/2-x, 1/2+y, z$).

Atoms	Distance	σ	Atoms	Distance	σ
Br—C7	1.878	(8)	C5—C6	1.391	(12)
S—O1	1.503	(6)	C5—C12	1.511	(13)
S—C2	1.830	(9)	C6—C7	1.379	(12)
S—C9	1.803	(8)	C6—H4	0.959	(108)
N—C3	1.496	(10)	C7—C8	1.431	(10)
N—C5	1.351	(10)	C8—C9	1.399	(10)
N—C9	1.361	(10)	C10—H5	1.008	(115)
O2—C8	1.263	(10)	C10—H6	0.996	(114)
O3—C11	1.212	(11)	C10—H7	0.832	(109)
O4—C11	1.305	(10)	C12—H8	1.075	(103)
O4—H1	0.965	(107)	C12—H9	0.943	(114)
C2—C3	1.515	(11)	C12—H10	0.776	(115)
C2—C10	1.523	(13)	O2—O4'	2.460	(8)
C2—H2	0.936	(110)	O2—H1'	1.537	(104)
C3—C11	1.544	(12)	S—O4'	3.039	(8)
C3—H3	0.986	(110)	S—H1'	2.675	(110)

The configuration relative to the plane of the pyridine ring is given in Table 5, in which are listed the distances from all atoms of the molecule to the least squares plane through the atoms of the pyridine ring. It is seen that the sulfoxide oxygen atom O1 and the carboxyl group are on the same side of the least squares plane, whereas the methyl group around C10 attached to C2 is on the opposite side of this plane.

Table 4. Bond angles in degrees with their estimated standard deviations. Atoms designated with a prime belong to the neighbouring molecule ($3/2-x$, $1/2+y$, z).

Atoms	Angle	σ	Atoms	Angle	σ
O1-S-C2	108.7	(0.4)	Br-C7-C8	117.5	(0.6)
O1-S-C9	108.2	(0.4)	C6-C7-C8	122.7	(0.7)
C2-S-C9	86.9	(0.4)	O2-C8-C7	122.6	(0.7)
C3-N-C5	124.8	(0.6)	O2-C8-C9	124.9	(0.7)
C3-N-C9	113.3	(0.6)	C7-C8-C9	112.5	(0.7)
C5-N-C9	121.9	(0.6)	S-C9-N	112.6	(0.5)
C11-O4-H1	111.2	(6.1)	S-C9-C8	123.0	(0.6)
S-C2-C3	105.3	(0.5)	N-C9-C8	124.4	(0.7)
S-C2-C10	107.7	(0.6)	C2-C10-H5	119.0	(6.0)
S-C2-H2	104.7	(6.5)	C2-C10-H6	103.0	(6.3)
C3-C2-C10	115.6	(0.7)	C2-C10-H7	101.3	(7.5)
C3-C2-H2	115.3	(6.6)	H5-C10-H6	83.0	(9.2)
C10-C2-H2	107.5	(6.8)	H5-C10-H7	129.4	(9.7)
N-C3-C2	105.1	(0.6)	H6-C10-H7	118.0	(10.4)
N-C3-C11	110.5	(0.6)	O3-C11-O4	126.5	(0.8)
N-C3-H3	108.8	(6.0)	O3-C11-C3	123.3	(0.7)
C2-C3-C11	115.1	(0.7)	O4-C11-C3	110.2	(0.7)
C2-C3-H3	114.0	(6.3)	C5-C12-H8	104.1	(5.9)
C11-C3-H3	103.4	(6.1)	C5-C12-H9	111.9	(7.3)
N-C5-C6	117.6	(0.7)	C5-C12-H10	107.7	(9.3)
N-C5-C12	119.8	(0.7)	H8-C12-H9	118.9	(8.7)
C6-C5-C12	122.5	(0.8)	H8-C12-H10	109.3	(10.4)
C5-C6-C7	120.8	(0.7)	H9-C12-H10	104.5	(11.3)
C5-C6-H4	112.5	(6.7)	C8-O2-H1'	119.2	(4.2)
C7-C6-H4	126.8	(6.7)	O2-H1'-O4'	158.4	(10.1)
Br-C7-C6	119.8	(0.6)			

Table 5. Distances in Å from the least squares plane through the atoms of the pyridine ring. Atoms marked with an asterisk are those defining the plane.

Atom	Distance	Atom	Distance	Atom	Distance
Br	-0.10	*C5	0.01	H2	-0.47
S	0.08	*C6	0.01	H3	-0.63
*N	-0.02	*C7	-0.02	H4	0.02
O1	1.52	*C8	0.01	H5	-2.66
O2	0.05	*C9	0.01	H6	-2.54
O3	2.23	C10	-2.20	H7	-2.33
O4	1.30	C11	1.30	H8	0.13
C2	-0.69	C12	-0.01	H9	0.57
C3	-0.09	H1	1.92	H10	-0.72

The shortest intermolecular distance between non-hydrogen atoms is the one between the hydroxyl oxygen atom O2 and O4', one of the oxygen atoms of the carboxyl group in a neighbouring molecule ($3/2-x$, $1/2+y$, z). This distance is only 2.46 Å, which strongly suggests hydrogen bonding. An equiv-

alent configuration occurs between O4 in the reference molecule and O2'' in another neighbouring molecule ($3/2 - x, -1/2 + y, z$). H1 is the hydrogen atom to be involved in the hydrogen bond. The distances from this atom to the two oxygen atoms in question are 1.0 Å and 1.5 Å. Since both distances are considerably shorter than the distance corresponding to van der Waals contact (2.6 Å), this is to be considered a hydrogen bond by the Hamilton-Ibers criterion.⁵

The angle of the hydrogen bond is found to be 158°, but the estimated standard deviation is about 10°. It is possible that the sulfur atom has some effect on the hydrogen bond, since the distances S-O4' and S-H1' are only 3.04 Å and 2.7 Å, respectively. However, any detailed discussion of hydrogen bonding in this structure is hardly justifiable on the basis of X-ray diffraction data.

The remaining intermolecular distances are all about or larger than the sums of the van der Waals radii. We may conclude that the molecules are linked *via* hydrogen bonds thus forming infinite chains which are held together by weaker intermolecular forces.

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