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7,8-Dihydro-8-hydroxy-2-methyl-3*H*,6*H*-[1,3]thiazino[3,2-*b*][1,2,4]triazine-3-one

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Abstract. $C_7H_9N_3O_2S$, M.W. 199·26, space group $P2_1/c$, monoclinic, $a=9{\cdot}770(6)$, $b=9{\cdot}601(8)$, $c=11{\cdot}198(8)$ Å, $\beta=125{\cdot}6(4)^\circ$ (from oscillation and Weissenberg photographs), $Z=4$, $D_x=1{\cdot}542$, $D_m=1{\cdot}54(1)$ g cm^{-3} (by flotation), $\mu=31{\cdot}7$ cm^{-1}. The molecules located along the same screw axes are held together by hydrogen bonds, forming infinite chains along **b**. The high-temperature parameters of the oxygen atom of the hydroxyl group are probably due to rapid tautomeric changes.

Introduction. The title compound forms needles (needle axis *b*); its preparation was described by Hornyák, Láng, Lempert & Menczel (1969). Weissenberg photographs were taken with a Nonius camera and unfiltered Cu *K* radiation of the layers *h*0*l*–*h*5*l* and *hk*0–*hk*5. No cutting of the needles was possible without damage, and the photographs of the different axes were made with crystals of approximately the same dimensions (0·1 × 0·6 × 0·05 mm). No absorption corrections were made and, in view of the large influence of absorption on the intensities of the *c* axis photographs, only those around **b** were used for intensity measurements and for interlayer scaling (Menczel, Samay & Simon, 1972). 1038 independent reflexions (357 with zero intensity) were measured by visual estimation. The structure was solved by direct methods: the program *MULTAN* of Main, Woolfson & Germain (1970) produced 8 sets of signs for 155 reflexions with $E > 1{\cdot}5$. An E map calculated with the set of signs with highest figures of merit revealed peaks for 10 of the 13 non-hydrogen atoms; a subsequent electron density synthesis revealed the positions of all non-hydrogen atoms. The resulting structure-factor calculation, with an overall temperature factor $B=2{\cdot}6$ Å^2 given by a Wilson plot, resulted in $R=0{\cdot}39$ for the observed data. After 6 cycles of block-diagonal least-squares calculation with individual isotropic and 4 cycles with anisotropic thermal parameters, the refinement was terminated at $R=0{\cdot}156$ for the observed and $R=0{\cdot}170$ for all reflexions. The intensities of the non-observed reflexions were taken as half the minimum measured value. 64 reflexions were left out of the refinement, on account of extinction or uncertainty of the intensity measurement. A difference map did not give the hydrogen positions, but a low peak in the vicinity of C(8) suggested that H and OH were possibly statistically inverted at this asymmetrical carbon atom. On this assumption, we tried to explain the surprisingly high temperature parameters of O(13). Further refinement of the structure with different proportions of the two kinds of asymmetrical carbon configurations did not result in

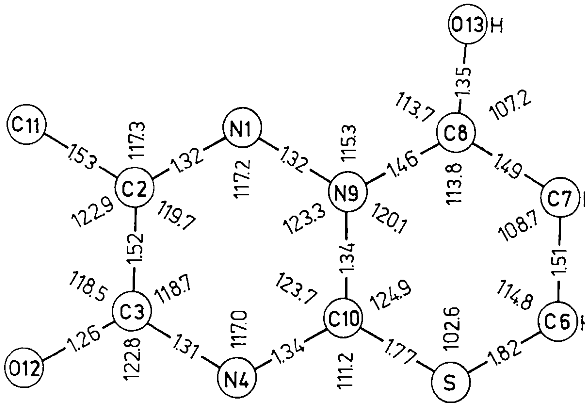

Fig. 1. Bond lengths and angles. The e.s.d.'s for bond lengths vary from 0·018 to 0·027 Å, those for bond angles from 1·3 to 2·0°.

Table 1. *Final fractional atomic coordinates* (× 10^4) *and thermal parameters* (× 10^4) *with estimated standard deviations in parentheses*

(*a*) Fractional coordinates

	x	*y*	*z*
S	8153 (4)	4655 (6)	6249 (3)
O(12)	3157 (18)	4543 (23)	1246 (13)
O(13)	8146 (18)	1046 (26)	6293 (15)
N(1)	4417 (13)	1900 (22)	3951 (11)
N(4)	5430 (16)	4520 (23)	3609 (13)
N(9)	5801 (12)	2533 (20)	5016 (10)
C(2)	3462 (15)	2568 (24)	2688 (11)
C(3)	4035 (20)	3970 (27)	2487 (15)
C(6)	9039 (16)	3474 (26)	7806 (12)
C(7)	7789 (19)	2473 (27)	7723 (15)
C(8)	6936 (16)	1685 (26)	6315 (13)
C(10)	6321 (17)	3756 (25)	4844 (12)
C(11)	1793 (25)	1890 (32)	1493 (18)

Table 1 (*cont.*)

(*b*) Thermal parameters. The B_{ij} coefficients are given by $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})]$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	97 (3)	48 (10)	59 (2)	−43 (10)	62 (4)	10 (8)
O(12)	211 (18)	201 (40)	94 (9)	−93 (46)	151 (18)	101 (33)
O(13)	185 (19)	377 (45)	102 (12)	234 (43)	53 (23)	−143 (35)
N(1)	62 (12)	148 (36)	113 (7)	13 (32)	33 (13)	13 (26)
N(4)	121 (16)	85 (35)	77 (10)	−64 (36)	70 (19)	22 (30)
N(9)	86 (11)	76 (29)	50 (7)	12 (29)	83 (12)	−15 (23)
C(2)	88 (13)	77 (38)	45 (8)	58 (34)	77 (15)	25 (26)
C(3)	120 (18)	121 (43)	62 (10)	74 (43)	69 (20)	95 (33)
C(6)	93 (13)	134 (42)	42 (8)	−110 (36)	67 (14)	1 (28)
C(7)	158 (17)	56 (41)	95 (10)	−68 (42)	164 (18)	−41 (33)
C(8)	106 (16)	71 (38)	69 (9)	−19 (40)	108 (16)	−11 (30)
C(10)	103 (16)	134 (43)	42 (8)	−7 (38)	73 (15)	58 (28)
C(11)	165 (27)	108 (47)	76 (14)	65 (57)	50 (30)	0 (41)

lower thermal parameters of O(13), but increased *R*. The final atomic parameters are listed in Table 1. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Fig. 1 shows the bond lengths and angles, Fig. 2 an *ORTEP* stereo drawing (Johnson, 1965) of the molecule, and Fig. 3 the projection of one half of the unit cell (two molecules related by screw-axis symmetry), viewed along **a**. A table of F_o and F_c values is available.*

Discussion. The aim of this structure determination was to confirm the structural formula [Fig. 4(*a*)], deduced from chemical evidence. In spite of the high e.s.d.'s of the bond lengths and angles due to the low number of reflexions, the alternative isomeric structure [Fig. 4(*b*)] could definitively be ruled out. Moreover some additional aspects of the structure could be determined. Ring *A* is planar, the distances of the atoms forming the ring from the least-squares best plane are less than 0·01 Å. C(11) and O(12) are slightly out of the plane (both by 0·08 Å, in opposite directions). Ring *B* has the boat form. A hydrogen bond of 2·75 Å connects the O(13)H hydroxyl group with O(12′) of the adjacent molecule lying on the same screw axis, and molecules of adjoining screw axes form enantiomeric infinite chains. The values of the angles at O(13) and O(12′) (112·1 and 168·2° respectively) indicate that the hydrogen atom is situated on the O(13)–O(12′) axis. In ring *A* the C–N and N–N bond lengths are between the single and double-bond values (1·47 and 1·25 Å respectively: Wells, 1962) and are approximately equal, their mean value, 1·327 Å, being near to the C–N bond length in *s*-triazine (1·338 Å: Lancaster & Stoicheff, 1956) (1·319 Å: Wheatley, 1955). Similar C–N values have been found in homopyrimidazole derivatives (1·322, 1·326, 1·339 Å: Simon & Sasvári, 1972; Sasvári & Simon, 1973). Structural chemical considerations suggest that some differences in bond lengths can be taken as significant, with a probability higher than that given by normal significance-test calculations. Noteworthy is the shortening of the C(3)–N(4) bond adjacent to the carbonyl group. Of the two carbon–sulphur bonds, C(6)–S is close to 1·817 Å, the average of the carbon–sulphur single-bond

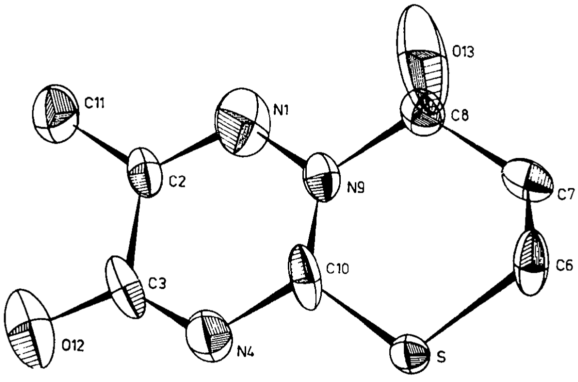

Fig. 2. *ORTEP* stereo drawing (Johnson, 1965) of the molecule.

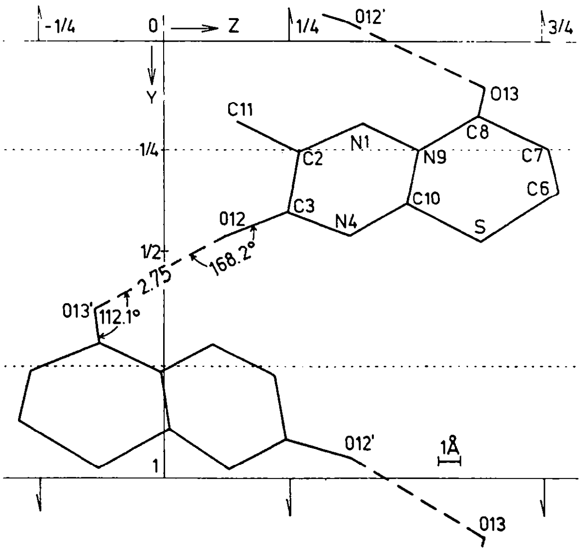

Fig. 3. Projection of one half of the unit cell (two molecules related by a screw axis) viewed along **a**.

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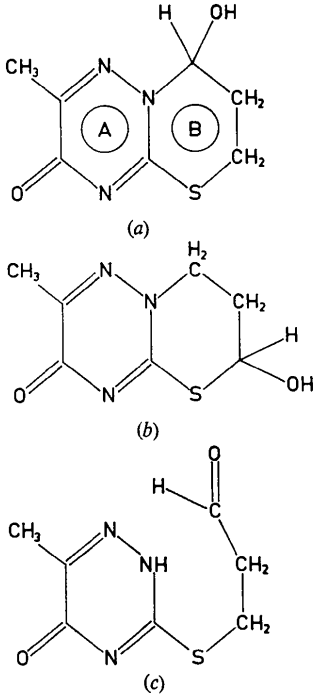
length in saturated acyclic and heterocyclic compounds (Sutton, 1965), while the length of C(10)–S is approximately equal to the C(sp^2)–S bond lengths in phenothiazine (1·770 Å: Freeman, 1968) and in diethazine (1·765 Å: Marsau, 1971). The sulphur atom lies nearly in the plane of ring *A* (deviation 0·04 Å). C(8)–N(9) is a normal single bond; the deviation of C(8) from the plane of ring *A* is 0·21 Å. The C–C bonds of the molecule are normal single bonds, but those in ring *B* show some shortening comparable with other saturated ring structures (*e.g.* Sasvári & Simon, 1973). The coordination around C(6), C(7) and C(8) is probably tetrahedral. The C(3)–O(12) bond is slightly lengthened compared with the C=O double bond in ketones (1·215 Å: Sutton, 1965), and the C(8)–O(13) bond is considerably shortened compared with the C–O single bond (1·426 Å: Sutton, 1965).



(*a*)

(*b*)

(*c*)

Fig. 4. Chemical formulae of the title compound: (*a*) the confirmed structure, (*b*) the alternative isomeric structure ruled out by the present investigation, (*c*) open-chain tautomeric form.

The most interesting feature of the molecular structure of Fig. 4(*a*) is the high thermal motion of O(13), the maximum elongation of the thermal ellipsoid coinciding with the C(8)–O(13) axis. Although according to its IR and UV spectra (Hornyák *et al.*, 1969), the title compound exists, both in the crystal and in solution, practically as the pure tautomer of Fig. 4(*a*), the existence of minor amounts of the open-chain tautomer Fig. 4(*c*) are not excluded. On the assumption of rapid ring–chain tautomerism $4(a)\rightleftharpoons 4(c)$ (with the equilibrium considerably shifted towards the left), the shape of the thermal ellipsoid of O(13) and the shortening of the C(8)–O(13) bond may be explained. Attempts to verify this assumption are in progress.

The calculations were performed on the ODRA 1304 computer at the Computing Centre of the Faculty of Sciences of the L. Eötvös University; the authors wish to express their thanks to the staff of the Computing Centre. We wish to thank to Dr Gy. Argay for the *ORTEP* stereo drawing.

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