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## Structure of 6-Chloro-3,4-dihydro-1H-2,3-benzothiazine 2,2-Dioxide

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**Abstract.** C<sub>8</sub>H<sub>8</sub>ClNO<sub>2</sub>S,  $M_r = 217.68$ , monoclinic,  $P2_1/c$ ,  $a = 10.860$  (2),  $b = 9.849$  (9),  $c = 9.360$  (3) Å,  $\beta = 113.00$  (5)°,  $V = 921$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.569$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 5.94$  cm<sup>-1</sup>,  $F(000) = 448$ ,  $T = 293$  K,  $R = 0.043$  for 1061 observed reflections. The heterocyclic ring adopts a half-chair conformation. There are two hydrogen bonds between molecules related by (i)  $1 - x, 1 - y, z$  [N(3)⋯O(1<sup>i</sup>) 3.047 (5), H(31)⋯O(1<sup>i</sup>) 2.22 (5) Å and N—H⋯O 156 (4)°] and (ii)  $1 - x, 1 - y, 1 - z$  [C(4)⋯O(2<sup>ii</sup>) 3.42 (5), H(41)⋯O(1<sup>ii</sup>) 2.494 (6) Å and N—H⋯O 163.4 (4)°]. There is a short contact between Cl(1) and O(2) of the molecules related by (iii)  $1 + x, y, 1 + z$  [Cl(1)⋯O(2<sup>iii</sup>) 3.050 (3) Å].

**Experimental.** The synthesis of the title compound has been reported previously (Orazi, Corral & Bravo, 1986). Crystals were obtained by slow cooling (330–300 K) of a chloroform solution. The crystal used for data collection had dimensions  $0.1 \times 0.15 \times 0.2$  mm.

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Intensities were measured with a Nonius CAD-4 diffractometer in  $\omega$ - $2\theta$  scan mode, with scan width  $(0.80 + 0.35 \tan \theta)^\circ$  and scan speed  $2.50$ – $6.67^\circ \text{ min}^{-1}$ , and using graphite-monochromated Mo  $K\alpha$  radiation. Unit-cell parameters were determined from a least-squares fit of the setting angles of 23 reflections with  $20.5 < 2\theta < 42.5^\circ$ . Data were collected for  $-1 < h < 11$ ,  $0 < k < 11$ ,  $-12 < l < 12$ , and to  $\theta_{\text{max}} = 23^\circ$ . One standard reflection (32 $\bar{6}$ ) varied by  $\pm 1.9\%$  of the mean intensity over data collection. 2064 reflections were measured, of which 1616 were unique ( $R_{\text{int}} = 0.011$ ) and 1061 were considered unobserved on the criterion  $I > 3\sigma(I)$ . Lorentz-polarization and geometrical absorption corrections were applied (for the latter the average transmission factor was 0.88, with maximum 0.91 and minimum 0.83 for  $\bar{1}20$  and  $\bar{1},11,0$  reflections, respectively). The structure was solved by (centrosymmetric) direct methods and the model refined by least squares. The H atom of the NH group was placed at a position based on that found in a difference synthesis and refined with a particular isotropic thermal parameter. Other H atoms were placed geometrically (C—H 0.96 Å), and constrained to ride on their C atoms, with two common isotropic thermal parameters for CH<sub>2</sub> and fused-benzene H atoms, respectively. Full-

Table 1. Fractional positional parameters for non-H atoms and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j \quad (\text{Hamilton, 1959}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
C(1)	0.6312 (3)	0.7009 (4)	0.2116 (4)	4.1 (1)
S(2)	0.4976 (1)	0.5973 (1)	0.2067 (1)	3.88 (3)
O(1)	0.4000 (3)	0.5872 (3)	0.0513 (3)	5.40 (8)
O(2)	0.4551 (3)	0.6401 (3)	0.3259 (3)	5.05 (9)
N(3)	0.5681 (3)	0.4509 (3)	0.2555 (4)	4.03 (9)
C(4)	0.6783 (4)	0.4451 (4)	0.4096 (4)	4.2 (1)
C(5)	0.8900 (4)	0.5523 (4)	0.5848 (4)	4.6 (1)
C(6)	0.9765 (4)	0.6600 (5)	0.6333 (4)	5.0 (1)
C(7)	0.9530 (4)	0.7774 (6)	0.5537 (5)	6.1 (2)
C(8)	0.8392 (4)	0.7895 (4)	0.4199 (5)	5.2 (1)
C(9)	0.7500 (4)	0.6835 (4)	0.3641 (4)	3.8 (1)
C(10)	0.7747 (3)	0.5633 (4)	0.4492 (4)	3.68 (9)
Cl(1)	1.1228 (1)	0.6411 (2)	0.8018 (1)	7.47 (5)

Table 2. Bond distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

C(1)—S(2)	1.760 (4)	C(1)—C(9)	1.515 (4)
S(2)—O(1)	1.430 (2)	S(2)—O(2)	1.428 (4)
S(2)—N(3)	1.613 (4)	N(3)—C(4)	1.472 (4)
N(3)—H(31)	0.88 (5)	C(4)—C(10)	1.512 (5)
C(5)—C(10)	1.396 (4)	C(6)—C(7)	1.345 (7)
C(9)—C(10)	1.393 (5)	C(5)—C(6)	1.371 (6)
C(7)—C(8)	1.379 (6)	C(8)—C(9)	1.381 (5)
C(6)—Cl(1)	1.757 (3)		
S(2)—C(1)—C(9)	110.4 (3)	S(2)—N(3)—C(4)	115.2 (3)
S(2)—N(3)—H(31)	110 (3)	C(4)—N(3)—H(31)	117 (3)
C(7)—C(8)—C(9)	121.7 (5)	C(1)—S(2)—O(1)	110.1 (2)
N(3)—C(4)—C(10)	115.5 (4)	C(1)—C(9)—C(8)	119.0 (3)
C(1)—S(2)—O(2)	108.9 (2)	C(6)—C(5)—C(10)	119.7 (4)
C(1)—C(9)—C(10)	122.5 (3)	C(4)—C(10)—C(5)	116.9 (3)
C(1)—S(2)—N(3)	102.5 (2)	C(5)—C(6)—C(7)	121.6 (3)
C(8)—C(9)—C(10)	118.5 (3)	O(1)—S(2)—O(2)	118.6 (2)
O(1)—S(2)—N(3)	107.9 (2)	C(7)—C(6)—Cl(1)	119.8 (3)
C(4)—C(10)—C(9)	123.6 (3)	O(2)—S(2)—N(3)	107.8 (2)
C(6)—C(7)—C(8)	119.1 (4)	C(5)—C(10)—C(9)	119.3 (3)
C(5)—C(6)—Cl(1)	118.5 (3)		

matrix least-squares refinement, with all non-H atoms anisotropic, was performed, minimizing  $\sum [w(|F_o| - |F_c|)^2]$ , where  $w = [\sigma^2(F_o) + 0.005F_o^2]^{-1}$ . A total of 125 parameters were refined. Refinement converged to final  $R = 0.043$ ,  $wR = 0.049$  and  $S = 0.818$  ( $R = 0.083$ ,  $wR = 0.0949$  and  $S = 1.23$  for all data). Inspection of  $F_c$  and  $F_o$  values indicated a need for a correction for secondary extinction,  $F_{corr} = F_c / [1.0 - 10^{-4} \chi F_c^2 / \sin \theta]$ , where  $\chi = 0.0239$  in the final run. Final  $(\Delta/\sigma)_{max} = 0.03$ ;  $\Delta\rho_{min} = -0.36$  and  $\Delta\rho_{max} = 0.27 \text{ e \AA}^{-3}$  in the final difference map. Atomic scattering factors for non-H atoms were taken from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970); those for H atoms were taken from Stewart, Davidson & Simpson (1965). Most of the calculations were performed on MicroVAX II computer at the Departamento de Física de la Universidad Nacional de La Plata; programs used were *SHELX76* (Sheldrick, 1976), *SHELXS86* (Sheldrick, 1985) and *ORTEP* (Johnson, 1965). Fractional atomic parameters with equivalent isotropic thermal

parameters for the non-H atoms are given in Table 1.\* The numbering scheme is shown in Fig. 1. The molecules pack in the unit cell in the manner shown in the stereoscopic diagram of Fig. 2. Table 2 shows selected bond lengths and angles within the molecule.

**Related literature.** This is the fourth 2,3-benzothiazine we have structurally characterized (Rivero, Bianchet & Bravo, 1991*a,b*, 1993). The  $\text{SO}_2$  group geometry [ $\text{O—S—O } 118.6(2)^\circ$ ], S—C distance [ $1.760(4) \text{ \AA}$ ] and deviations from planarity of the heterocyclic ring are in agreement with those of previously studied structures in this series and with the values reported for related compounds, such as  $\beta$ -sulphanilamide (O'Connell & Maslen, 1967) and sulthiame, containing a thiazine ring without fused benzene (Aupers, Carlisle & Lindley, 1974; Camerman & Camerman, 1975). However, the S—N distance [ $1.613(4) \text{ \AA}$ ] is closer to that in the unsubstituted compound [ $1.603(4) \text{ \AA}$  (Rivero, Bianchet & Bravo, 1991*a*)] and smaller than those in the other compounds with substitution of the H atom on the

\* Lists of structure factors, least-squares planes, H-atom parameters, anisotropic thermal parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55560 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR0195]

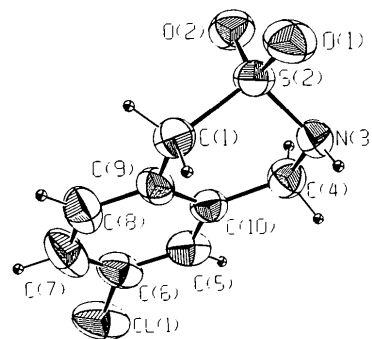


Fig. 1. Perspective drawing of the title compound indicating the atom labeling. Thermal ellipsoids are drawn at the 50% probability level.

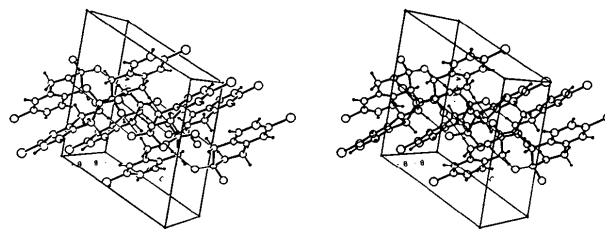


Fig. 2. Stereoscopic view of the unit cell. Thin lines represent the hydrogen bonds between molecules.

N atom {[N-methyl and 3-(*p*-chlorophenyl)]-3,4-dihydro-1*H*-2,3-benzothiazine 2,2-dioxide, 1.634 (6) and 1.641 (4) Å, respectively (Rivero, Bianchet & Bravo, 1991*b*, 1993)}. The S—N length is considerably shorter than the normal single-bond value of 1.67–1.68 Å, which indicates electron delocalization within the SN group. A search of the July 1991 edition of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) showed that no other 2,3-benzothiazine structures have been reported. However, 1,2-benzothiazines are relatively common (Kojić-Prodić & Ružić-Toroš, 1982; Norris, Berke & Lombardino, 1985; Golić & Leban, 1987).

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## Structure of 4-Methylpyridinium Bromide

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**Abstract.**  $\gamma$ -Picolinium bromide, [C<sub>6</sub>H<sub>7</sub>NH]Br,  $M_r$  = 174.05, monoclinic,  $Cm$ ,  $a$  = 8.785 (4),  $b$  = 8.318 (3),  $c$  = 4.920 (1) Å,  $\beta$  = 103.62 (3)°,  $V$  = 349.4 (4) Å<sup>3</sup>,  $Z$  = 2,  $D_x$  = 1.654 g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.71073 Å,  $\mu$  = 57.23 cm<sup>-1</sup>,  $F(000)$  = 172,  $T$  = 293 K,  $R$  = 0.033

for 415 reflections with  $F_o^2 > 3\sigma(F_o^2)$  and 41 variables. The compound consists of C<sub>6</sub>H<sub>7</sub>NH<sup>+</sup> cations and Br<sup>-</sup> anions. Both species reside on crystallographic mirror planes defined by the Br, N(1), C(4), C(7) and H(71) atoms. The Br—N distance is 3.12 (1) Å.

\* This work was performed while the author held a National Research Council–NASA Research Associateship.

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**Experimental.** The title compound was prepared in the following manner. Under argon, a solution of