

Structure of 3-(*p*-Chlorophenyl)-3,4-dihydro-1*H*-2,3-benzothiazine 2,2-Dioxide

BY BLAS E. RIVERO* AND MARIO A. BIANCHET†

Departamento de Física Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 y 115, CC. 67 (1900), La Plata, Argentina

AND RODOLFO D. BRAVO

Departamento de Química Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 y 115, CC. 67 (1900), La Plata, Argentina

(Received 23 August 1991; accepted 21 July 1992)

Abstract. $C_{14}H_{12}ClNO_2S$, $M_r = 293.77$, monoclinic, $P2_1/c$, $a = 11.269$ (3), $b = 14.095$ (5), $c = 8.508$ (5) Å, $\beta = 100.01$ (6)°, $V = 1331$ (2) Å³, $Z = 4$, $D_x = 1.466$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.437$ mm⁻¹, $F(000) = 608$, $T = 293$ K, $R = 0.0399$ for 910 observed reflections. The thiazine heterocyclic ring is in a half-chair conformation. The chlorophenyl-group plane is almost perpendicular [91.0 (2)°] to the benzene ring of the benzothiazine portion. The chlorophenyl rings are stacked along the *c* direction with C—Cl bonds alternately oriented along the *b* direction.

Experimental. The synthesis of the title compound has been reported previously (Orazi, Corral & Bravo, 1986). The crystal used for data collection had dimensions 0.05 × 0.2 × 0.4 mm, and was obtained by slow cooling (330–300 K) of an ethanol solution. Intensities were measured with a Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation, using ω - 2θ scans of width (0.80 + 0.35tan θ)° and speed 2.50–6.67° min⁻¹. Unit-cell parameters were determined from a least-squares fit of the setting angles of 25 reflections with $9.44 < 2\theta < 19.5^\circ$. Data were collected for $-12 < h < 12$, $0 < k < 15$, $0 < l < 9$, and to $\theta_{\text{max}} = 23^\circ$. One standard reflection (404) showed no significant change in intensity over data collection. 2402 reflections were measured, of which 1587 were unique ($R_{\text{int}} = 0.025$) and 910 were considered observed on the criterion $I > 3\sigma(I)$. Lorentz-polarization and geometrical absorption corrections were applied (for the latter the average transmission factor was 0.96, with maximum 0.97 and minimum 0.93 for 010 and 001 reflections, respectively). The structure was solved by

(centrosymmetric) direct methods and refined by least squares. The H atoms were placed in positions calculated geometrically (C—H 0.96 Å), and constrained to ride on their C atoms, with two common isotropic thermal parameters for CH₂ and benzene H atoms, respectively. Full-matrix least-squares refinement, with all non-H atoms anisotropic, was performed, minimizing $\sum[w(|F_o| - |F_c|)^2]$, where $w = [\sigma^2(F_o) + 0.0002F_o^2]^{-1}$. 175 parameters were refined. Excluding unobserved reflections, $R = 0.0384$, $wR = 0.0367$ and $S = 1.271$. Inspection of F_c and F_o values indicated the need for a correction for secondary extinction, $F_{\text{corr}} = F_c / [1.0 - 10^{-4}\chi F_c^2 / \sin\theta]$, where $\chi = 0.0067$ in the final run. Final $(\Delta/\sigma)_{\text{max}} = 0.001$; $\Delta\rho_{\text{min}} = -0.16$ and $\Delta\rho_{\text{max}} = 0.20$ e Å⁻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. Fig. 2 shows a stereoscopic view of the unit cell. Table 2 shows bond lengths and angles.

Related literature. The bond lengths and angles of the title compound are in good agreement with those

‡ Lists of structure factors, least-squares planes, anisotropic thermal parameters, torsion angles and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55561 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR0194]

* Member of Carrera del Investigador Científico, CICPBA, Argentina.

† Present address: Department of Biophysics and Biophysical Chemistry, Johns Hopkins University, School of Medicine, 725 N. Wolfe St, Baltimore, MD 21205 USA.

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

$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$ (Hamilton, 1959).

	x	y	z	B_{eq}
C(1)	-0.4073 (4)	0.3768 (4)	-0.0752 (7)	3.7 (2)
S(2)	-0.2929 (1)	0.4584 (1)	-0.0027 (2)	3.66 (5)
O(1)	-0.2463 (3)	0.4374 (3)	0.1612 (4)	4.5 (1)
O(2)	-0.3345 (3)	0.5525 (2)	-0.0476 (5)	4.6 (1)
N(3)	-0.1891 (3)	0.4327 (3)	-0.1094 (5)	3.3 (2)
C(4)	-0.2314 (4)	0.4479 (4)	-0.2818 (6)	4.0 (2)
C(5)	-0.3862 (5)	0.4017 (4)	-0.5142 (8)	4.4 (2)
C(6)	-0.4981 (6)	0.3704 (4)	-0.5864 (8)	5.1 (2)
C(7)	-0.5803 (6)	0.3406 (4)	-0.4912 (8)	5.0 (2)
C(8)	-0.5504 (5)	0.3453 (4)	-0.3293 (8)	4.4 (2)
C(9)	-0.4362 (5)	0.3766 (3)	-0.2560 (7)	3.4 (2)
C(10)	-0.3535 (5)	0.4053 (3)	-0.3503 (7)	3.4 (2)
C(11)	-0.1134 (4)	0.3510 (4)	-0.0601 (7)	3.1 (2)
C(12)	-0.1425 (4)	0.2614 (4)	-0.1209 (7)	3.7 (2)
C(13)	-0.0693 (5)	0.1854 (4)	-0.0655 (7)	4.2 (2)
C(14)	0.0312 (5)	0.1986 (4)	0.0474 (7)	3.9 (2)
C(15)	0.0631 (4)	0.2876 (4)	0.1049 (8)	4.5 (2)
C(16)	-0.0103 (4)	0.3640 (4)	0.0491 (7)	4.1 (2)
Cl(1)	0.1188 (1)	0.1022 (1)	0.1230 (2)	6.08 (7)

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

C(1)—S(2)	1.758 (5)	C(1)—C(9)	1.516 (8)
S(2)—O(1)	1.433 (4)	S(2)—O(2)	1.436 (3)
S(2)—N(3)	1.641 (4)	N(3)—C(4)	1.478 (6)
C(4)—C(10)	1.521 (7)	C(5)—C(6)	1.376 (8)
C(5)—C(10)	1.380 (9)	C(6)—C(7)	1.40 (2)
C(7)—C(8)	1.362 (9)	C(8)—C(9)	1.400 (8)
C(9)—C(10)	1.391 (9)	N(3)—C(11)	1.451 (7)
C(11)—C(12)	1.382 (8)	C(11)—C(16)	1.369 (7)
C(12)—C(13)	1.384 (8)	C(13)—C(14)	1.364 (7)
C(14)—C(15)	1.372 (8)	C(14)—Cl(1)	1.737 (6)
C(15)—C(16)	1.390 (7)		
S(2)—C(1)—C(9)	111.9 (4)	S(2)—N(3)—C(4)	112.3 (3)
C(1)—C(9)—C(10)	122.5 (5)	C(1)—S(2)—O(1)	109.2 (3)
O(1)—S(2)—O(2)	119.9 (3)	N(3)—C(4)—C(10)	115.9 (4)
C(8)—C(9)—C(10)	119.4 (5)	C(1)—S(2)—O(2)	109.0 (2)
C(6)—C(5)—C(10)	121.7 (6)	C(4)—C(10)—C(5)	117.9 (5)
C(1)—S(2)—N(3)	102.2 (2)	C(5)—C(6)—C(7)	119.1 (7)
C(4)—C(10)—C(9)	123.1 (5)	C(6)—C(7)—C(8)	120.0 (6)
C(5)—C(10)—C(9)	118.9 (5)	O(1)—S(2)—N(3)	108.5 (3)
C(7)—C(8)—C(9)	120.8 (6)	O(2)—S(2)—N(3)	106.7 (2)
C(1)—C(9)—C(8)	118.1 (5)	S(2)—N(3)—C(11)	117.1 (4)
C(4)—N(3)—C(11)	118.3 (4)	N(3)—C(11)—C(16)	118.6 (5)
N(3)—C(11)—C(12)	121.8 (5)	C(11)—C(12)—C(13)	119.4 (4)
C(11)—C(16)—C(15)	120.9 (5)	C(12)—C(11)—C(16)	119.7 (5)
C(12)—C(13)—C(14)	120.5 (5)	C(13)—C(14)—Cl(1)	120.3 (4)
C(13)—C(14)—C(15)	120.7 (6)	C(14)—C(15)—C(16)	118.9 (5)
C(15)—C(14)—Cl(1)	119.1 (5)		

of other 2,3-benzothiazines published previously by us (Rivero, Bianchet & Bravo, 1991). The S—N distance [1.641 (4) \AA] is longer than that found in 1*H*-3,4-dihydro-2,3-benzothiazine [1.603 (4) \AA], nearer to that with methyl substitution [1.634 (6) \AA] and in agreement with those reported for related compounds, such as β -sulphanilamide (O'Connell & Maslen, 1967) and sulthiame, containing a thiazine ring without fused benzene (Aupers, Carlisle & Lindley, 1974; Camerman & Camerman, 1975). The C—Cl distance [1.737 (6) \AA] is in agreement with

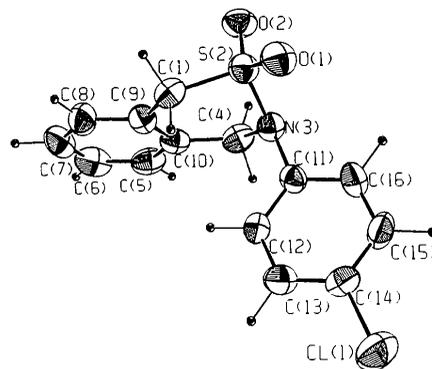


Fig. 1. Perspective drawing of the title compound indicating atom labeling. Thermal ellipsoids are drawn at the 50% probability level.

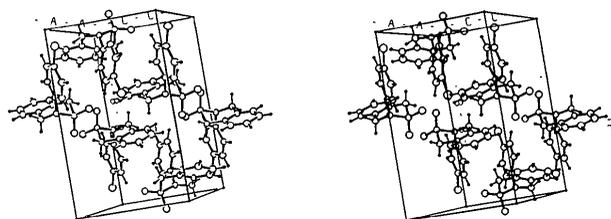


Fig. 2. A stereoscopic view of the unit cell.

other compounds such as *p*-chloro-*trans*-cinnamic acid and β -(*p*-chlorophenyl)propionic acid [1.741 and 1.747 \AA , respectively (Glusker, Zacharias & Carrell, 1975)]. 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; Golič & Leban, 1987).

This work received partial support from CONICET and CICPBA, Argentina, and from CNPq, Brazil, through a CONICET—CNPq exchange program. The utilization of National Cancer Institute, Frederick Cancer Research Facility, Advanced Scientific Computing Laboratory (ASCL) facilities for the Cambridge Structural Database search is gratefully acknowledged.

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

BY BLAS E. RIVERO* AND MARIO A. BIANCHET†

Departamento de Física Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 y 115, CC. 67 (1900), La Plata, Argentina

AND RODOLFO D. BRAVO

Departamento de Química Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 y 115, CC. 67 (1900), La Plata, Argentina

(Received 6 September 1991; accepted 29 June 1992)

Abstract. C₈H₈ClNO₂S, $M_r = 217.68$, monoclinic, $P2_1/c$, $a = 10.860$ (2), $b = 9.849$ (9), $c = 9.360$ (3) Å, $\beta = 113.00$ (5)°, $V = 921$ (1) Å³, $Z = 4$, $D_x = 1.569$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 5.94$ cm⁻¹, $F(000) = 448$, $T = 293$ 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(1ⁱ) 3.047 (5), H(31)⋯O(1ⁱ) 2.22 (5) Å and N—H⋯O 156 (4)°] and (ii) $1 - x, 1 - y, 1 - z$ [C(4)⋯O(2ⁱⁱ) 3.42 (5), H(41)⋯O(1ⁱⁱ) 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(2ⁱⁱⁱ) 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.

* Member of Carrera del Investigador Científico, CICPBA, Argentina.

† Present address: Department of Biophysics and Biophysical Chemistry, Johns Hopkins University, School of Medicine, 725 N. Wolfe St, Baltimore, MD 21205, USA.

Intensities were measured with a Nonius CAD-4 diffractometer in ω - 2θ 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 CH₂ and fused-benzene H atoms, respectively. Full-