Acta Cryst. (1989). C**45**, 1905–1908

Structural Studies on Benzothiadiazine Derivatives: 3-Amino-4*H*-1,2,4-benzothiadiazine 1,1-Dioxide and 3-Hydrazino-4*H*-1,2,4-benzothiadiazine 1,1-Dioxide

By G. Bombieri and F. Demartin

Istituto Chimico Farmaceutico, Università di Milano, Viale Abruzzi 42, 20131 *Milano, Italy*

and D. Braghiroli, S. Todeschi and M. Di Bella

Dipartimento di Scienze Farmaceutiche, Università di Modena, Via S. Eufemia 19, 41100 *Modena, Italy*

(*Received* 28 *December* 1988; *accepted* 8 *March* 1989)

Abstract. 3-Amino-4*H*-1,2,4-benzothiadiazine 1,1-dioxide (1), $C_7H_7N_3O_2S$, $M_r = 197{\cdot}22$, monoclinic, *Cc*, $a = 14{\cdot}259\,(2)$, $b = 22{\cdot}539\,(3)$, $c = 8{\cdot}741\,(3)$ Å, $\beta = 114{\cdot}10(2)°$, $V = 2564\,(2)$ Å^3, $Z = 12$, $D_x = 1{\cdot}532$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 3·311 cm^{-1}, $F(000) = 1224$, $T = 293$ K, $R = 0{\cdot}040$, $wR = 0{\cdot}051$, 2132 observed reflections. 3-Hydrazino-4*H*-1,2,4-benzothiadiazine 1,1-dioxide (2), $C_7H_8N_4O_2S$, $M_r = 212{\cdot}24$, monoclinic, $P2_1/n$, $a = 6{\cdot}976(4)$, $b = 8{\cdot}403(3)$, $c = 14{\cdot}748\,(3)$ Å, $\beta = 90{\cdot}25\,(3)°$, $V = 864(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}631$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 3·362 cm^{-1}, $F(000) = 440$, $T = 293$ K, $R = 0{\cdot}042$, $wR = 0{\cdot}048$, 1147 observed reflections. The benzothiadiazine ring is almost planar in both compounds with the sulfonyl group perpendicular to the rings. The 4*H*-isomer is found in both structures which are characterized by electron delocalization extended mainly towards the substituent in the 3 position. In compound (2) an intramolecular hydrogen bond is present [N(6)—H(N4) 2·21 Å].

Introduction. In the course of research into the interaction of benzothiadiazine derivatives with receptor systems in the CNS, crystallographic determinations were carried out on (1) and (2), as part of a program undertaken in order to study the effect of changing the substituents, both in the heterocyclic ring and in the aromatic ring, on the molecular parameters and conformation of benzothiadiazines.

Experimental. (1) was prepared as described in the literature (Raffa, Melegari & Vampa, 1966). Recrystallization from ethyl alcohol gave crystals suitable for X-ray diffraction. A colorless needle, 0·1 × 0·1 × 0·4 mm, was aligned on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Intensities were collected to $2\theta = 50°$ (*h*: − 16 to 16; *k*: 0 to 26; *l*: 0 to 10). The diffracted intensities were corrected for Lorentz and polarization, but not for absorption. The cell dimensions were taken from a least-squares fit to 25 reflections in the range $18 \leq 2\theta \leq 30°$. The space group *Cc* was determined by systematic absences and by structure solution and refinement. Of the 2476 reflections measured, 2132 were considered as observed having $I \geq 2\sigma(I)$. No crystal decay was observed during data collection. The structure was solved by direct methods using *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and refined by full-matrix least squares with anisotropic temperature factors for N, O and S atoms, and isotropic ones for carbons. In the final difference Fourier map the H-atom positions were clearly localized but because of the large number of parameters they were introduced at calculated positions (C—H and N—H 0·95 Å) with fixed isotropic $U = 0{\cdot}05$ Å^2 for the H—C and 0·04 Å^2 for the H—N. The final *R* was 0·040 and *wR* was 0·051 for 245 variable parameters ($S = 2{\cdot}0$). Compound (2), prepared according to the literature (Raffa, Di Bella, Melegari & Vampa, 1962), was crystallized from water in the form of pale yellow plate-like transparent crystalls. A crystal 0·1 × 0·2 × 0·2 mm was chosen for data collection. Intensities were collected to $2\theta = 50°$ (*h*: −8 to 8; *k*: 0 to 10; *l*: 0 to 17); no deterioration was noted. The procedure used for data collection and structure solution was as for (1). The 127 parameters refined include the coordinates and anisotropic thermal parameters for all non-H atoms. H-atom positions were clearly detected in the final difference Fourier map but were introduced at calculated positions as in (1). Final *R* factors for 1147 reflections with $I \geq 2\sigma(I)$ of the 1681 collected were $R = 0{\cdot}042$ and $wR = 0{\cdot}048$ ($S = 1{\cdot}5$). Weights assigned to individual observations were $w = 1/[\sigma(F_o)]^2$, where $\sigma(F_o) = [\sigma^2(I) + (0{\cdot}041)^2]^{1/2}/2F_o\mathrm{Lp}$. Final maximum Δ/σ 0·04 for each structure; maximum $|\Delta\rho|$ excursions less than 0·41 and 0·28 e Å^{-3} for (1) and (2) respectively. The calculations were performed on a PDP 11/34 computer using the *SDP-Plus Structure Determination*

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Package (B. A. Frenz & Associates Inc., 1980). Atomic scattering factors were from *International Tables for X-ray Cyrstallography* (1974).

Discussion. Final atomic positions and equivalent or isotropic thermal parameters for non-H atoms are given in Tables 1 and 2,* while interatomic distances and valence angles are in Tables 3 and 4.

The least-squares planes were calculated on three distinct sections of the molecules: (*a*) the thiadiazine ring, (*b*) the benzene ring and (*c*) the sulfonic group. The two rings are planar (dihedral angles range from 1 to 2°), while the sulfonic group is perpendicular to the rest of the molecule (the values range from 89 to 91°).

Compound (1) has three molecules in the asymmetric unit, differing only in orientation with respect to the crystallographic axes. An *ORTEP* view (Johnson, 1976) of a molecule with the atom-numbering scheme is shown in Fig. 1. A comparison of bond distances and angles in the different molecules shows no significant differences (maximum $\Delta/\sigma = 1·8$) among equivalent structural parameters and, for this reason, in the *Discussion* the averaged value for each parameter has been taken. There is a significant difference in the two distances N(2)—C(3) 1·320 (4) and C(3)—N(4) 1·349 (4) Å, while C(3)—N(3) is 1·324 (5) Å. These values suggest a significant mesomeric effect along the N(2)—C(3)—N(3) fragment rather than inside the thiadiazine ring. In 7-chloro-3-methyl-1,2,4-benzothiadiazine 1,1-dioxide (Bandoli & Nicolini, 1977) the N(2)—C(3) and C(3)—N(4) bond distances are 1·300 (9) and 1·335 (9) Å respectively. This indicates a shortening of the two bonds with a higher double-bond character for the N(2)—C(3) distance.

The N(4)—C(9) bond length of 1·376 (4) Å, when compared to the corresponding value of 1·398 (9) Å in the methyl derivative previously quoted, and the values of the bond distances involving the N atoms of the thiadiazine ring, indicate for (1) a higher degree of electron delocalization which is enhanced by the presence of the amino group in the 3 position with respect to the methyl group in the quoted example.

A slightly distorted tetrahedral geometry is observed about sulfur. Angle O(1)—S—O(2) [112·4 (2)°] is slightly larger than the ideal tetrahedral value, while the other values are close to 109°. The two bond distances S—O(1) and S—O(2) of 1·448 (3) and 1·439 (3) Å respectively are comparable to the values reported in sulfones and other thio-oxides (Alléaume, Gulko, Herbstein, Kapon & Marsh, 1976, and references therein; Bandoli & Nicolini, 1977; Desiraju & Kamala, 1983).

Table 1. *Positional parameters with e.s.d.'s in parentheses, for* (1)

	x	*y*	*z*	*B*(Å²)
S(*A*)	0·265	0·23883 (5)	0·099	3·07 (2)
S(*B*)	0·28643 (8)	0·42074 (4)	0·7796 (2)	3·07 (2)
S(*C*)	0·50271 (8)	0·15954 (4)	0·7573 (2)	3·05 (2)
O(1*A*)	0·3221 (2)	0·2710 (2)	0·2519 (5)	4·27 (8)
O(1*B*)	0·2095 (2)	0·4331 (2)	0·8437 (5)	4·24 (7)
O(1*C*)	0·4183 (3)	0·1754 (2)	0·6025 (5)	4·44 (9)
O(2*A*)	0·3308 (2)	0·2045 (2)	0·0443 (5)	4·45 (8)
O(2*C*)	0·5232 (3)	0·2041 (1)	0·8863 (5)	4·32 (8)
O(2*B*)	0·3049 (3)	0·4708 (2)	0·6937 (5)	4·45 (8)
N(2*B*)	0·2517 (3)	0·3652 (2)	0·6616 (6)	3·9 (1)
N(2*C*)	0·6032 (3)	0·1491 (2)	0·7296 (6)	3·94 (9)
N(2*A*)	0·1993 (3)	0·2840 (2)	−0·0399 (6)	3·9 (1)
N(3*B*)	0·2665 (3)	0·2716 (2)	0·5793 (6)	3·90 (9)
N(3*A*)	0·0514 (3)	0·3235 (2)	−0·2293 (5)	4·0 (1)
N(3*C*)	0·7367 (3)	0·0952 (2)	0·7273 (6)	4·06 (9)
N(4*B*)	0·3946 (3)	0·3058 (2)	0·8217 (5)	3·05 (8)
N(4*C*)	0·6210 (3)	0·0480 (2)	0·8059 (5)	3·02 (8)
N(4*A*)	0·0388 (3)	0·2422 (2)	−0·0826 (5)	2·99 (8)
C(3*C*)	0·6519 (3)	0·0978 (2)	0·7549 (5)	2·77 (7)*
C(3*A*)	0·0979 (3)	0·2827 (2)	−0·1151 (5)	2·70 (7)*
C(3*B*)	0·3042 (3)	0·3154 (2)	0·6887 (5)	2·70 (7)*
C(5*B*)	0·5387 (4)	0·3332 (2)	1·0754 (6)	3·63 (9)*
C(5*A*)	0·0075 (4)	0·1565 (2)	0·0547 (6)	3·64 (9)*
C(5*C*)	0·5085 (3)	−0·0101 (2)	0·8890 (6)	3·74 (9)*
C(6*B*)	0·5876 (4)	0·3735 (3)	1·1990 (7)	4·8 (1)*
C(6*A*)	0·0437 (4)	0·1117 (3)	0·1700 (7)	4·7 (1)*
C(6*C*)	0·4227 (4)	−0·0148 (3)	0·9222 (7)	4·7 (1)*
C(7*B*)	0·5443 (5)	0.4280 (3)	1·2026 (8)	5·7 (1)*
C(7*A*)	0·1469 (5)	0·1067 (3)	0·2708 (8)	5·7 (1)*
C(7*C*)	0·3638 (5)	0·0344 (3)	0·9152 (8)	5·5 (1)*
C(8*B*)	0·4501 (4)	0·4424 (3)	1·0743 (7)	4·8 (1)*
C(8*A*)	0·2155 (4)	0·1461 (3)	0·2524 (7)	4·8 (1)*
C(8*C*)	0·3886 (4)	0·0884 (3)	0·8670 (7)	4·9 (1)*
C(9*B*)	0·4437 (3)	0·3465 (2)	0·9463 (5)	2·77 (7)*
C(9*A*)	0·0749 (3)	0·1973 (2)	0·0337 (5)	2·75 (8)*
C(9*C*)	0·5354 (3)	0·0438 (2)	0·8403 (5)	2·78 (7)*
C(10*A*)	0·1795 (3)	0·1906 (2)	0·1321 (5)	3·10 (8)*
C(10*B*)	0·4018 (3)	0·4020 (2)	0·9470 (6)	3·22 (8)*
C(10*C*)	0·4732 (3)	0·0927 (2)	0·8276 (6)	3·15 (8)*

* Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 2. *Positional parameters with e.s.d.'s in parentheses, for* (2)

	x	*y*	*z*	*B*(Å²)*
S	0·7051 (1)	0·25790 (9)	0·10162 (5)	2·20 (1)
O(1)	0·8549 (3)	0·1642 (3)	0·1435 (1)	3·11 (5)
O(2)	0·5198 (3)	0·1813 (3)	0·0991 (2)	3·01 (5)
N(2)	0·6913 (4)	0·4224 (3)	0·1532 (2)	2·78 (6)
N(4)	0·7186 (4)	0·5811 (3)	0·0210 (2)	2·30 (5)
N(5)	0·6480 (4)	0·6900 (3)	0·1587 (2)	2·66 (6)
N(6)	0·6624 (4)	0·8394 (3)	0·1173 (2)	3·09 (6)
C(3)	0·6859 (4)	0·5608 (4)	0·1104 (2)	2·00 (6)
C(5)	0·8137 (5)	0·4942 (4)	−0·1280 (2)	2·88 (7)
C(6)	0·8595 (5)	0·3731 (5)	−0·1859 (2)	3·46 (8)
C(7)	0·8649 (5)	0·2171 (4)	−0·1577 (2)	3·31 (7)
C(8)	0·8228 (5)	0·1790 (4)	−0·0684 (2)	2·92 (7)
C(9)	0·7685 (4)	0·4592 (4)	−0·0379 (2)	2·11 (6)
C(10)	0·7718 (4)	0·3022 (4)	−0·0097 (2)	2·06 (6)

* Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

The distance C(10)—S is 1·745 (4) Å, shorter than the value quoted for a C(sp^3)—S single bond (1·8 Å)

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* Lists of H-atom positions, anisotropic vibrational amplitudes and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52031 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected bond distances* (Å) *and angles* (°) *for* (1)

	A	*B*	*C*	Averaged values
S—O(1)	1·446 (3)	1·449 (3)	1·449 (3)	1·448 (3)
S—O(2)	1·437 (3)	1·438 (3)	1·441 (3)	1·439 (3)
S—N(2)	1·568 (3)	1·568 (3)	1·565 (3)	1·567 (3)
N(2)—C(3)	1.322 (4)	1.318 (4)	1·320 (4)	1·320 (4)
C(3)—N(4)	1·348 (4)	1·355 (4)	1·345 (4)	1·349 (4)
N(4)—C(9)	1·377 (4)	1·376 (4)	1·374 (4)	1·376 (4)
C(9)—C(5)	1·395 (5)	1·396 (5)	1·392 (5)	1·394 (5)
C(5)—C(6)	1·370 (6)	1·365 (6)	1·372 (5)	1·369 (6)
C(6)—C(7)	1·377 (7)	1·381 (6)	1·376 (6)	1·378 (6)
C(7)—C(8)	1·379 (7)	1·391 (7)	1·381 (7)	1·384 (7)
C(8)—C(10)	1·391 (6)	1·385 (6)	1·387 (6)	1·388 (6)
C(10)—S	1·745 (4)	1·749 (4)	1·741 (4)	1·745 (4)
C(10)—C(9)	1·393 (5)	1·387 (5)	1·392 (5)	1·391 (5)
C(3)—N(3)	1·319 (5)	1·326 (5)	1·328 (5)	1·324 (5)
O(1)—S—O(2)	112·4 (2)	112·3 (2)	112·6 (2)	112·4 (2)
O(1)—S—N(2)	108·8 (2)	108·8 (2)	108·6 (2)	108·7 (2)
O(1)—S—C(10)	109·0 (2)	109·0 (2)	109·0 (2)	109·0 (2)
O(2)—S—N(2)	111·0 (2)	111·0 (2)	111·0 (2)	111·0 (2)
O(2)—S—C(10)	108·4 (2)	108·4 (2)	108·4 (2)	108·4 (2)
C(10)—S—N(2)	107·1 (2)	107·1 (2)	107·0 (2)	107·1 (2)
S—N(2)—C(3)	123·9 (3)	124·0 (3)	123·9 (3)	123·9 (3)
N(2)—C(3)—N(4)	124·1 (3)	124·2 (3)	124·4 (3)	124·2 (3)
C(3)—N(4)—C(9)	125·2 (3)	124·9 (3)	124·8 (3)	125·0 (3)
N(4)—C(9)—C(5)	120·9 (3)	120·6 (3)	120·6 (3)	120·7 (3)
C(9)—C(5)—C(6)	120·7 (4)	120·7 (4)	120·9 (4)	120·8 (4)
C(5)—C(6)—C(7)	120·9 (4)	121·4 (4)	120·6 (4)	121·0 (4)
C(6)—C(7)—C(8)	119·7 (5)	118·8 (5)	119·7 (4)	119·4 (5)
C(7)—C(8)—C(10)	119·5 (4)	119·6 (4)	119·8 (4)	119·6 (4)
C(8)—C(10)—S	120·5 (3)	120·2 (3)	120·6 (3)	120·4 (3)
S—C(10)—C(9)	118·4 (3)	118·3 (3)	118·4 (3)	118·4 (3)
C(8)—C(10)—C(9)	121·1 (4)	121·5 (4)	121·0 (4)	121·2 (4)
C(10)—C(9)—N(4)	121·2 (3)	121·6 (3)	121·4 (3)	121·4 (3)
C(10)—C(9)—C(5)	118·0 (3)	117·8 (3)	118·0 (3)	118·0 (3)
N(2)—C(3)—N(3)	118·0 (3)	118·2 (3)	117·6 (3)	117·9 (3)
N(4)—C(3)—N(3)	117·9 (3)	117·6 (3)	118·0 (3)	117·8 (3)

Table 4. *Selected bond distances* (Å) *and angles* (°) *for* (2)

S—O(1)	1·455 (2)	O(1)—S—O(2)	114·4 (1)
S—O(2)	1·444 (2)	O(1)—S—N(2)	108·4 (1)
S—N(2)	1·581 (2)	O(1)—S—C(10)	108·8 (1)
N(2)—C(3)	1·323 (3)	O(2)—S—N(2)	110·2 (1)
C(3)—N(4)	1·350 (3)	O(2)—S—C(10)	108·2 (1)
N(4)—C(9)	1·388 (3)	C(10)—S—N(2)	106·4 (1)
C(9)—C(5)	1·398 (4)	S—N(2)—C(3)	122·8 (2)
C(5)—C(6)	1·368 (4)	N(2)—C(3)—N(4)	124·9 (2)
C(6)—C(7)	1·376 (4)	C(3)—N(4)—C(9)	124·2 (2)
C(7)—C(8)	1·388 (4)	N(4)—C(9)—C(5)	119·8 (2)
C(8)—C(10)	1·397 (4)	C(9)—C(5)—C(6)	119·4 (3)
S—C(10)	1·748 (2)	C(5)—C(6)—C(7)	121·8 (3)
C(9)—C(10)	1·384 (3)	C(6)—C(7)—C(8)	120·1 (3)
C(3)—N(5)	1·326 (3)	C(7)—C(8)—C(10)	118·2 (3)
N(5)—N(6)	1·400 (3)	C(8)—C(10)—S	119·6 (2)
		S—C(10)—C(9)	118·8 (2)
		C(8)—C(10)—C(9)	121·6 (2)
		C(10)—C(9)—N(4)	121·2 (2)
		C(10)—C(9)—C(5)	118·9 (2)
		N(2)—C(3)—N(5)	118·0 (2)
		N(4)—C(3)—N(5)	117·1 (2)
		C(3)—N(5)—N(6)	119·0 (2)

(Khan, Taylor, Lehn & Dietrich, 1988, and references therein), which can be attributed to the difference between sp^2 and sp^3 carbon rather than to a partial double-bond character for C(10)—S. This observation has also been noted for the methyl derivative, where the corresponding value is 1·755 (7) Å. The short value of the N(2)—S bond distance of 1·567 (3) Å, also in agreement with the value of 1·599 (7) Å found in the methyl derivative, indicates partial double-bond character. The other values of the bond distances in the rings are indicative of some degree of electron delocalization also inside the ring. Finally, the localization of all the hydrogens in the structure allows us to conclude that the isomer studied here is 4*H*. The crystal packing is determined by van der Waals interactions (the intermolecular N···N contact distances are larger than 3·5 Å).

Compound (2) has a hydrazine group instead of an aminic one; an *ORTEP* view (Johnson, 1976) is given in Fig. 2. The presence of the bulkier substituent at position 3 does not make important changes in the molecular structure, which is comparable to that of (1).

The hydrazine moiety is oriented with the N(5) proton in the direction of N(2) [N(2)···H(N5) 2·47 Å], and N(6) probably with the lone pair pointing towards the N(4) proton [N(6)···H(N4) 2·21 Å]. The shorter value of this contact distance suggests the probable presence of an intramolecular hydrogen-bond interaction. This does not seem to influence the bond-distance values of N(2)—C(3) and C(3)—N(4), which are equal to the corresponding ones in (1).

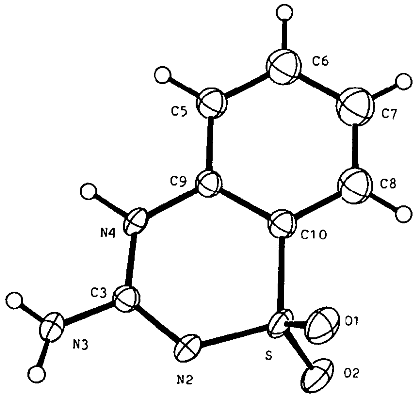

Fig. 1. An *ORTEP* view (Johnson, 1976) pf compound (1) (molecule *A*) showing 50% probability vibrational ellipsoids for non-H atoms.

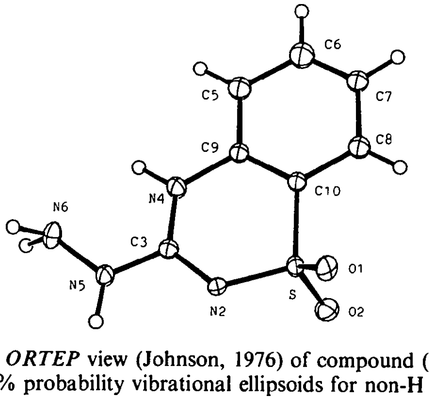

Fig. 2. An *ORTEP* view (Johnson, 1976) of compound (2) showing 50% probability vibrational ellipsoids for non-H atoms.

The N(5)—N(6) bond length of 1·400 (3) Å has the expected value for a single bond. The hydrazine moiety is slightly rotated with respect to the thiadiazine ring [the torsion angle N(6)—N(5)—C(3)—N(2) is 173°].

The other molecular dimensions are as in (1). The isomer is 4*H* in this case too. van der Waals contacts determine the molecular packing (the intermolecular N···N contact distances are larger than 3·5 Å).

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Acta Cryst. (1989). C45, 1908–1911

Structures of (±)-*trans*-4-(3-Nitrophenyl)- (I) and (+)-*trans*-4-(4-Fluorophenyl)-2-hydroxy-2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one (II)

BY VAN HENRY SAVELL JR AND EDWARD J. VALENTE

Department of Chemistry, Mississippi College, Clinton, MS 39058, USA

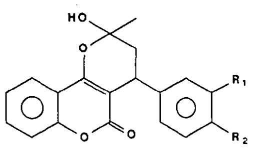
AND DRAKE S. EGGLESTON

Department of Physical and Structural Chemistry, Smith, Kline & French Laboratories, King of Prussia, PA 19406, USA

(*Received* 21 *July* 1988; *accepted* 22 *March* 1989)

Abstract. Derivatives of 2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one. (I) Racemic *trans*-2-hydroxy-4-(3-nitrophenyl), $C_{19}H_{15}NO_6$, $M_r = 353·33$, triclinic, $P\overline{1}$, $a = 12·468$ (1), $b = 14·531$ (3), $c = 9·218$ (2) Å, $\alpha = 99·00$ (2), $\beta = 98·03$ (1), $\gamma = 84·35$ (1)°, $V = 1628·3$ (7) Å^3, $Z = 4$, $D_x = 1·441$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 8·679$ cm^{-1}, $F(000) = 736$, $T = 294$ K, final $R = 0·042$ for 4981 observations [$I \geq 3\sigma(I)$]. The asymmetric unit contains two enantiomeric molecules [(2*R*,4*R*) and (2*S*,4*S*)] unrelated by crystallographic symmetry, and differing slightly in conformation. Hydrogen bonding occurs between a donor hydroxyl on one enantiomer (*A*) and a receptor carbonyl oxygen on another (*B*), O···O = 2·752 (2) Å, and between a donor hydroxyl (*B*) and a receptor hydroxyl (*A*), O···O = 2·923 (2) Å. Dihydropyran rings adopt half-chair conformations distorted toward the *d*,*e*-diplanar conformation. (II) Resolved (2*R*,4*R*)-(+)-*trans*-2-hydroxy-4-(4-fluorophenyl), $C_{19}H_{15}FO_4$, $M_r = 326·32$, orthorhombic, $P2_12_12_1$, $a = 9·838$ (4), $b = 10·817$ (3), $c = 14·777$ (6) Å, $V = 1572·6$ (17) Å^3, $Z = 4$, $D_x = 1·374$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 8·351$ cm^{-1}, $F(000) = 680$, $T = 294$ K, final $R = 0·040$ for all 1583 observations. Hydroxyls are hydrogen bonded intermolecularly to carbonyl groups, O···O = 2·745 (3) Å. The embedded dihydropyran ring adopts a half-chair conformation.

Introduction. Dihydropyran ring conformations can be studied through solid state structures of a series of crystalline warfarin analogs containing the embedded heterocycle. This contribution describes the structures of two substituted 4-aryl derivatives of 2-hydroxy-2-methyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one.



(I) $R_1 = NO_2$ $R_2 = H$
(II) $R_1 = H$ $R_2 = F$

Solutions of warfarin analogs consist of an equilibrium mixture of two diastereomeric hemiketals and the intermediate keto form. They crystallize as

0108-2701/89/121908-04$03.00