The H(—N) atoms were refined freely, while a riding model was used for all other H atoms, with $U(\mathrm{H}) = 1.2U_{eq}(\mathrm{C})$.

Data collection: *XSCANS* (Siemens, 1994*a*). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*94 (Sheldrick, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

.The project had been supported by the Hoechst AG, the Deutsche Forschungsgemeinschaft, the State of Hesse and the Fond der Chemischen Industrie.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1289). Services for accessing these data are described at the back of the journal.

References

Bock, H., Dienelt, R., Schoedel, H. & Havlas, Z. (1995). *Tetrahedron Lett.* **43**, 7855–7858.

Bock, H., Dienelt, R., Schoedel, H., Havlas, Z., Herdtweck, E. & Herrmann, W. A. (1993). *Angew. Chem.* **105**, 1826–1828; *Angew. Chem. Int. Ed. Engl.* **32**, 1758–1760.

Colvin, E. W., Beck, A. K., Bastani, B., Seebach, D., Yasushi, K. & Dunitz, J. D. (1980). *Helv. Chim. Acta*, **63**, 697–710.

Konowalow, M. (1896). *Ber. Dtsch Chem. Ges.* **29**, 2193–2198.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1994). *SHELXS94. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994*a*). *XSCANS User's Manual.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994*b*). *XP. Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1999). C**55**, 1149–1152

Pyridinium and 1,2-diazinium salts of chloranilic acid

Hiroyuki Ishida and Setsuo Kashino

Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan. E-mail: ishidah@cc.okayama-u.ac.jp

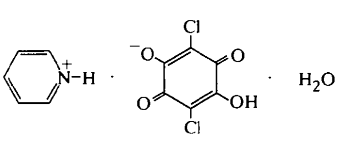
(*Received 23 October 1998; accepted 8 March 1999*)

Abstract

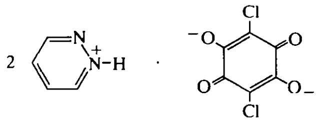
The crystal structures of two salts of chloranilic acid (2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone), namely pyridinium chloranilate monohydrate, $C_5H_6N^+\cdot C_6HCl_2O_4^-\cdot H_2O$, (I), and bis(1,2-diazinium) chloranilate, $2C_4H_5N_2^+\cdot C_6Cl_2O_4^{2-}$, (II), have been determined at room temperature. In (I) and (II), the cations and anions are held together by N—H···O hydrogen bonds with short N···O distances of 2.670 (4) Å in (I) and 2.582 (3) Å in (II). The H atom in the hydrogen bond in (I) was located at the N-atom site [N—H = 1.09 (5) and H···O = 1.70 (5) Å], while that in (II) was found near the center of N···O [N···H = 1.32 (5) and H···O = 1.28 (5) Å].

Comment

Several hydrogen-bonded complexes of the chloranilic acid–amine (1:1) system have been studied by IR (Issa *et al.*, 1991) and by IR, NMR and UV (Habeeb *et al.*, 1995). Habeeb *et al.* reported that the hydrogen bonds formed between chloranilic acid and amines vary from an N—H···O to an N···H—O type with decreasing pK_a values of the amines. The title compounds, (I) and (II), were investigated as part of a structural study on hydrogen bonding in chloranilic acid–amine systems. The pK_a values of pyridine and 1,2-diazine (pyridazine) are 5.2 and 2.3, respectively.



(I)



(II)

An asymmetric unit of (I) is composed of $C_5H_6N^+\cdot C_6HCl_2O_4^-\cdot H_2O$ and that of (II) is $C_4H_5N_2^+\cdot\frac{1}{2}C_6Cl_2O_4^{2-}$. The chloranilate ions in (I) and (II) show characteristic structures having four short C—C bonds

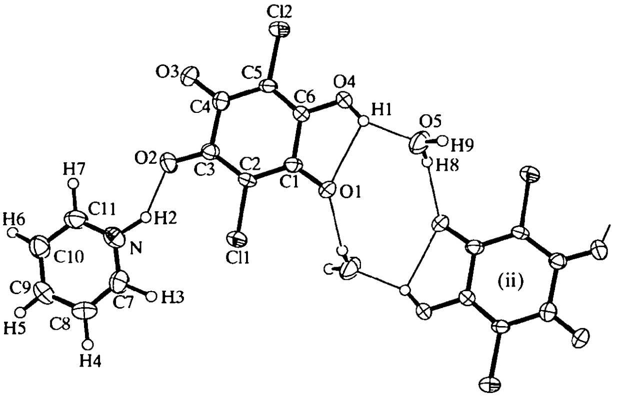


Fig. 1. *ORTEP*II (Johnson, 1976) view of (I), showing the atomic numbering. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms are drawn as spheres with $B_{iso} = 1.0$ Å^2. Hydrogen bonds are indicated by thin lines [symmetry code: (ii) $1 - x$, $1 - y$, $1 - z$].

[1.326 (4)–1.453 (4) Å] and two extremely long C—C bonds [1.521 (4)–1.547 (4) Å] (Tables 1 and 2), as reported for $2NH_4^+\cdot C_6Cl_2O_4^{2-}\cdot H_2O$ (Andersen, 1967). The N···O distances between the anions and cations are N···O2 = 2.670 (4) Å for (I) and N1···O2 = 2.582 (3) Å for (II), which are significantly shorter than the average N···O distance of 2.878 (3) Å in the N—H···O═C hydrogen bond (Taylor *et al.*, 1984), implying the formation of strong N—H···O hydrogen bonds in these salts. The H atom in the hydrogen bond in (I) was located at the N-atom site [N—H2 = 1.09 (5), H2···O2 = 1.70 (5) Å and N—H2···O2 = 145 (3)°] with a large displacement parameter [U_{iso} = 0.15 (2) Å^2], while that in (II) was found near the center of N···O [N1···H = 1.32 (5), H1···O2 = 1.28 (5) Å and N1···H1···O2 = 165 (4)°; U_{iso} = 0.16 (1) Å^2]. The fact that N—H distances in both salts are longer than the normal N—H bond (0.87 Å) and that the H atoms have large displacement parameters suggest that H2 in (I) and H1 in (II) are disordered in the hydrogen bonds.

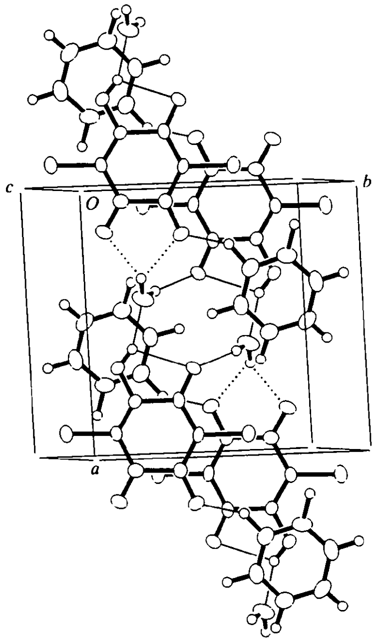


Fig. 2. Packing diagram of (I). Short N—H···O and O—H···O hydrogen bonds are indicated by thin lines, while long bifurcated O—H···O hydrogen bonds are indicated by dashed lines.

In (I), two O—H···O hydrogen bonds involving a water molecule [O4—H1 = 0.85 (4), H1···O5 = 1.81 (4) Å and O4—H1···O5 = 154 (4)°; O5—H8 0.75 (3), H8···O1^{ii} = 2.12 (3) Å and O5—H8···O1^{ii} = 169 (4)°; symmetry code: (ii) $1-x$, $1-y$, $1-z$] form a dimer of the asymmetric unit around a center of symmetry at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) (Fig. 1). The H1 atom attached to O4 also forms an intramolecular hydrogen bond with O1 [O4—H1 = 0.85 (4), H1···O1 = 2.24 (4) Å and O4—H1···O1 = 110 (3)°]. Bifurcated hydrogen bonds [O5—H9 = 0.91 (3), H9···O2^i = 2.23 (3) Å and O5—H9···O2^i = 136 (3)°; H9···O3^i = 2.17 (3) Å and O5—H9···O3^i = 145 (3)°; symmetry code: (i) $x-1$, y, z] combine the dimers, forming a three dimensional O—H···O hydrogen-bond network (Fig. 2). In (2), both ions are stacked in columns along the *a* axis (Fig. 3).

Experimental

The title compounds were prepared by mixing chloranilic acid with pyridine or pyridazine (1,2-diazine) (molar ratio 1:2) in CH_3CN. Single crystals were grown by slow evaporation of the solutions in CH_3CN at room temperature.

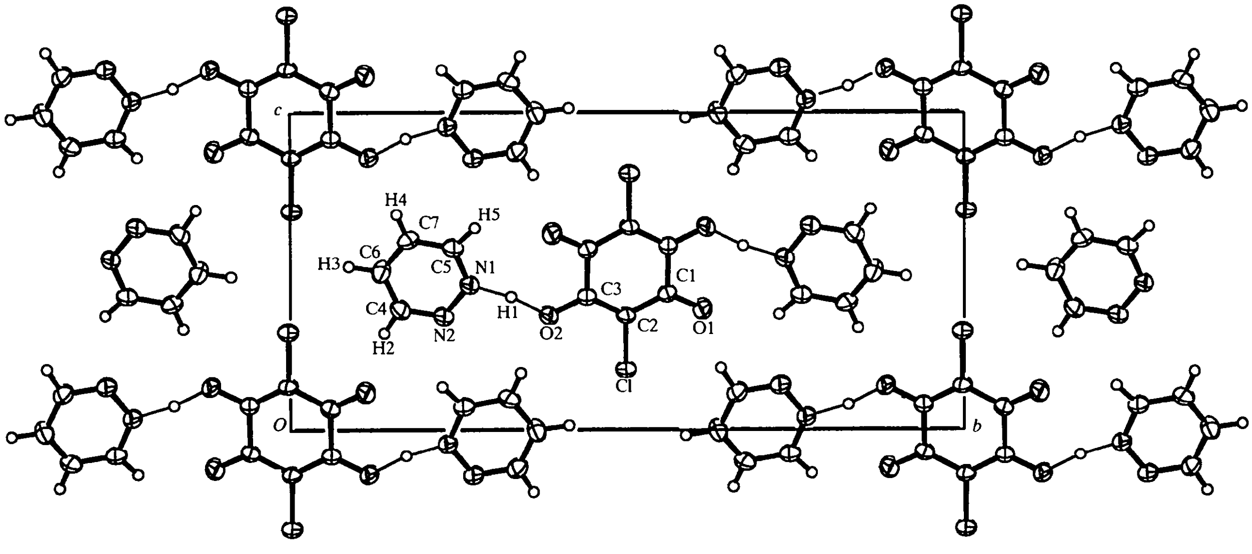


Fig. 3. Packing diagram of (II) viewed down the *a* axis, showing the atomic numbering. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms are drawn as spheres with B_{iso} = 1.0 Å^2. Hydrogen bonds are indicated by thin lines.

Compound (I)

Crystal data

$C_5H_6N^+ \cdot C_6HCl_2O_4^- \cdot H_2O$
$M_r = 306.10$
Triclinic
$P\overline{1}$
$a = 9.563\ (1)$ Å
$b = 9.657\ (1)$ Å
$c = 6.935\ (2)$ Å
$\alpha = 100.89\ (2)°$
$\beta = 102.54\ (2)°$
$\gamma = 90.26\ (1)°$
$V = 613.2\ (2)$ Å^3
$Z = 2$
$D_x = 1.658$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.8–11.5°$
$\mu = 0.544$ mm^{-1}
$T = 299$ K
Prismatic
0.15 × 0.15 × 0.15 mm
Dark brown

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: none
2985 measured reflections
2817 independent reflections
1577 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.022$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -9 \rightarrow 8$
3 standard reflections every 97 reflections intensity decay: 0.04%

Refinement

Refinement on F^2
$R(F) = 0.055$
$wR(F^2) = 0.049$
$S = 1.33$
2815 reflections
208 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o) + 0.00001|F_o|^2]$

$(\Delta/\sigma)_{\rm max} = 0.01$
$\Delta\rho_{\rm max} = 0.71$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.71$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (I)*

Cl1—C2	1.747 (3)	C1—C6	1.521 (4)
Cl2—C5	1.730 (3)	C2—C3	1.385 (4)
O1—C1	1.233 (4)	C3—C4	1.547 (4)
O2—C3	1.253 (3)	C4—C5	1.453 (4)
O3—C4	1.222 (3)	C5—C6	1.326 (4)
O4—C6	1.324 (3)	C7—C8	1.365 (5)
N—C7	1.334 (4)	C8—C9	1.384 (5)
N—C11	1.340 (4)	C9—C10	1.370 (5)
C1—C2	1.405 (4)	C10—C11	1.368 (5)
Cl1—C2—C3	118.3 (2)	C1—C2—C3	124.6 (3)
Cl1—C2—C1	117.1 (2)	C2—C3—C4	117.0 (3)
Cl2—C5—C6	120.7 (2)	C3—C4—C5	117.8 (3)
Cl2—C5—C4	117.6 (2)	C4—C5—C6	121.6 (3)
O1—C1—C2	126.8 (3)	C1—C6—C5	121.8 (3)
O1—C1—C6	116.6 (3)	C2—C1—C6	116.6 (3)
O2—C3—C2	127.4 (3)	N—C7—C8	120.1 (4)
O2—C3—C4	115.5 (3)	C7—N—C11	121.8 (3)
O3—C4—C3	118.9 (3)	C7—C8—C9	118.9 (3)
O3—C4—C5	123.3 (3)	C8—C9—C10	120.0 (3)
O4—C6—C1	115.9 (3)	C9—C10—C11	119.1 (4)
O4—C6—C5	122.2 (3)	N—C11—C10	120.0 (4)

Compound (II)

Crystal data

$2C_4H_5N_2^+ \cdot C_6Cl_2O_4^{2-}$
$M_r = 369.16$
Monoclinic
$P2_1/c$
$a = 3.799\ (1)$ Å
$b = 20.292\ (5)$ Å
$c = 9.675\ (2)$ Å
$\beta = 99.69\ (2)°$
$V = 735.1\ (3)$ Å^3
$Z = 2$
$D_x = 1.668$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.0–11.5°$
$\mu = 0.470$ mm^{-1}
$T = 293$ K
Prismatic
0.20 × 0.20 × 0.15 mm
Dark brown

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{\rm min} = 0.89$, $T_{\rm max} = 0.93$
1991 measured reflections
1739 independent reflections

1078 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 4$
$k = 0 \rightarrow 26$
$l = -12 \rightarrow 12$
3 standard reflections every 97 reflections intensity decay: 0.36%

Refinement

Refinement on F^2
$R(F) = 0.048$
$wR(F^2) = 0.061$
$S = 1.55$
1678 reflections
129 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o) + 0.00006|F_o|^2]$

$(\Delta/\sigma)_{\rm max} = 0.01$
$\Delta\rho_{\rm max} = 0.40$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.43$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (II)*

Cl—C2	1.737 (2)	C1—C2	1.423 (4)
O1—C1	1.224 (3)	C1—C3$^{\rm i}$	1.539 (3)
O2—C3	1.277 (3)	C2—C3	1.363 (4)
N1—N2	1.338 (3)	C4—C5	1.386 (4)
N1—C7	1.327 (3)	C5—C6	1.357 (4)
N2—C4	1.329 (3)	C6—C7	1.381 (4)
O1—C1—C2	124.6 (2)	C1—C3$^{\rm i}$—C2$^{\rm i}$	118.7 (2)
O1—C1—C3$^{\rm i}$	117.3 (3)	N2—N1—C7	122.7 (2)
C2—C1—C3$^{\rm i}$	118.1 (2)	N1—N2—C4	116.7 (2)
Cl—C2—C1	117.2 (2)	N2—C4—C5	123.4 (3)
Cl—C2—C3	119.6 (2)	C4—C5—C6	118.6 (2)
C1—C2—C3	123.2 (2)	C5—C6—C7	117.3 (3)
O2—C3—C1$^{\rm i}$	116.7 (2)	N1—C7—C6	121.3 (3)
O2—C3—C2	124.6 (2)		

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

X-ray measurements were made at the X-ray Laboratory of Okayama University. For both compounds, H atoms were found in a difference Fourier map and refined isotropically.

For both compounds, data collection: *MSC/AFC Diffractometer Control* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFC Diffractometer Control*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997–1998); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1993) and *PATTY* in *DIRDIF*92 (Beurskens *et al.*, 1992); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1082). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Andersen, E. K. (1967). *Acta Cryst.* **22**, 196–201.
Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.
Habeeb, M. M., Alwakil, H. A., El-Dissouky, A. & Fattab, H. A. (1995). *Pol. J. Chem.* **69**, 1428–1436.
Issa, Y. M., Darwish, N. A. & Hassib, H. B. (1991). *Egypt. J. Chem.* **34**, 87–93.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1990). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1997–1998). *TEXSAN for Windows* (Version 1.03) and *Single Crystal Structure Analysis Software* (Version 1.04). MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Taylor, R., Kennard, O. & Versichel, W. (1984). *Acta Cryst.* B**40**, 280–288.

Acta Cryst. (1999). C**55**, 1152–1154

7-Iodo-3-isopropylamino-4*H*-1,2,4-benzothiadiazine 1,1-dioxide

Léon Dupont,[a] Bernard Pirotte[b] and Pascal de Tullio[b]

[a]*Unité de Cristallographie, Institut de Physique B5, Université de Liège au Sart Tilman, B-4000 Liège, Belgium, and* [b]*Laboratoire de Chimie Pharmaceutique, Institut de Pharmacie F1, Université de Liège, Rue Fusch 5, B-4000 Liège, Belgium. E-mail: leon.dupont@ulg.ac.be*

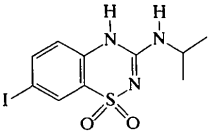
(*Received 24 November 1998; accepted 13 January 1999*)

Abstract

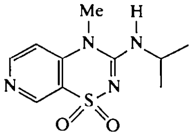
The title compound, $C_{10}H_{12}IN_3O_2S$, belongs to a new family of heterocyclic drugs developed as putative pancreatic B-cell ATP-sensitive potassium-channel openers. The crystal structure is compared with that of 3-isopropylamino-4-methyl-4*H*-pyrido[4,3-*e*][1,2,4]thiadiazine 1,1-dioxide and 3-isopropylamino-4*H*-pyrido-[4,3-*e*][1,2,4]thiadiazine 1,1-dioxide. The title compound adopts the 4*H*-tautomeric form, as in the corresponding pyridinic class of compounds.

Comment

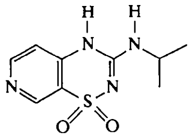
7-Iodo-3-isopropylamino-4*H*-1,2,4-benzothiadiazine 1,1-dioxide, (I), is an example of a new family of heterocyclic drugs, the 3-alkylamino-4*H*-1,2,4-benzothiadiazine 1,1-dioxides, structurally related to 3-alkylamino-4*H*-pyrido[4,3-*e*][1,2,4]thiadiazine 1,1-dioxides. The latter have been reported as powerful pancreatic B-cell ATP-sensitive potassium-channel (K_{ATP} channel) openers (Pirotte *et al.*, 1993, 1994; de Tullio *et al.*, 1996; Lebrun *et al.*, 1996). They are of great therapeutic interest as substitutes of diazoxide (7-chloro-3-methyl-4*H*-1,2,4-benzothiadiazine 1,1-dioxide) in the treatment of some pancreatic disorders characterized by an excess of insulin secretion. The 7-iodo-substituted compound was prepared in order to have a potential pharmacological tool for studying the K_{ATP} channels. Further work will investigate the possibility of labelling the 7-position of the heterocycle with a radioactive I atom.



(I)



(II)



(III)

The crystallographic study of (I) should help the structural comparison of 3-alkylamino-4*H*-1,2,4-benzothiadiazine 1,1-dioxides with their isosteric pyridines, for instance, with the structures of 3-isopropylamino-4-methyl-4*H*-pyrido[4,3-*e*][1,2,4]thiadiazine 1,1-dioxide [(II); Dupont *et al.*, 1996] and 3-isopropylamino-4*H*-pyrido[4,3-*e*][1,2,4]thiadiazine 1,1-dioxide [(III); de Tullio *et al.*, 1996]. In (II), a typical 4*H*-tautomeric form results from the presence of the methyl substituent at the 4-position of the thiadiazine 1,1-dioxide ring. The C3—N4 [1.381 (4) Å] and C3—N2 [1.326 (4) Å] distances in (II) are useful references with respect to C—N double- and single-bond length in such a ring system. The corresponding distances in (I) [1.367 (8) and 1.334 (9) Å] and (III) [1.366 (4) and 1.315 (4) Å] lead to the conclusion that the 4*H*-tautomeric form is also favoured in the crystalline state for that example of a benzothiadiazine 1,1-dioxide. It agrees with previous results observed in diazoxide (Bandoli & Nicolini, 1977). This is confirmed by the hydrogen-bonding scheme, which includes N4—H4 in (I) and (III). Moreover, there is no close intermolecular contact including N2 in the three crystal structures. The distance between H(C12) and a hypothetical H(N2) atom [2.12 and 2.14 Å in (I) and (III), respectively]