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7-Chloro-2-methyl-3-methylamino-2*H*-1,2,4-benzothiadiazine 1,1-dioxide

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The title compound, $C_9H_{10}ClN_3O_2S$, was prepared for structural comparison with analogous products known as myorelaxants and inhibitors of insulin release. The 2*H*-tautomeric form is imposed by the presence of a methyl group in the 2-position. There are four independent molecules (*A*, *B*, *C* and *D*) in the asymmetric unit which have almost the same geometry. The C—N distances in the four thiadiazine rings [C—N single- and double-bond mean values of 1.405 (3) and 1.304 (3) Å, respectively] may serve as reference to characterize the 2*H*-tautomeric form in analogous structures. The NH group of the methylamino substituent of each molecule participates in an intermolecular hydrogen bond with a sulfoxide O atom acting as acceptor. These four independent hydrogen bonds give rise to two types of infinite chains, both stretching along the *a* axis and having molecular compositions of ...*ABABAB*... and ...*CDCDCD*...

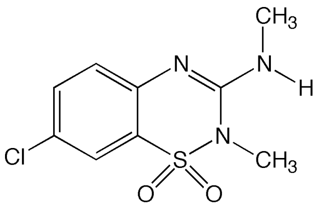
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.106
Data-to-parameter ratio = 10.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound is a structural analogue of diazoxide (7-chloro-3-methyl-4*H*-1,2,4-benzothiadiazine 1,1-dioxide; Bandoli & Nicolini, 1977) and other 3-alkylamino-7-chloro-4*H*-1,2,4-benzothiadiazine 1,1-dioxides known to exert important biological properties (smooth muscle myorelaxants and inhibitors of insulin release) like 7-chloro-(*R*/*S*)-3-[1-(cyclohexyl)ethylamino]-4*H*-1,2,4-benzothiadiazine 1,1-dioxide (Dupont *et al.*, 1999). A typical 2*H*-tautomeric form results from the presence of the methyl substituent in the 2-position of the thiadiazine ring. There are four independent molecules (*A*, *B*, *C* and *D*) in the asymmetric unit with essentially identical geometry: even the most flexible N2—C3—N11—C12 torsion angles do not deviate from the mean value of −172.7 (2)° by more than 2.1 (2)°. The C3—N2 (*A*—*D*) distances are within the range 1.402 (3)–1.408 (3) Å, and C3—N4 within 1.301 (3)–1.309 (3) Å. They are useful references with respect to C3—N2 single- and C3—N4 double-bond length in such a ring system. The corresponding distances in diazoxide are 1.300 (9) and 1.335 (9) Å, respectively, and 1.325 (5) and 1.368 (4) Å in 7-chloro-(*S*)-3-[1-(cyclohexyl)ethylamino]-4*H*-1,2,4-benzo-



(I)

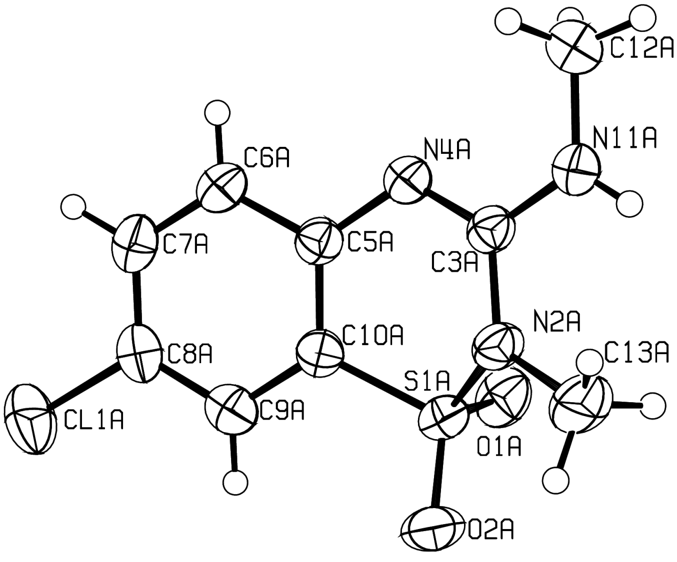


Figure 1
The molecular structure with atom-labelling scheme of molecule *A*. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

thiadiazine 1,1-dioxide (Dupont *et al.*, 1999). Typical values for C3—N2 double-bond [1.326 (4) Å] and C3—N4 single-bond [1.381 (4) Å] have been observed in the molecular structure of 3-isopropylamino-4-methyl-4*H*-pyrido[4,3-*e*][1,2,4]thiadiazine 1,1-dioxide (Dupont *et al.*, 1996) where a 4*H*-tautomeric form is imposed by a 4-methyl substituent.

The crystal packing is dominated by two symmetry independent types of hydrogen-bonded infinite chains. The chains of the first type are made up of alternating *A* and *B* molecules linked *via* N—H···O bonds formed by the methylamino NH groups and sulfoxide O atoms. The chains of the second type are built in an analogous way and involve alternating *C* and *D* molecules. Both chains stretch along the shortest axis, *i.e. a*, of the unit cell.

Experimental

A solution of 7-chloro-2-methyl-3-methylsulfanyl-2*H*-1,2,4-benzothiadiazine 1,1-dioxide [obtained as described in Di Bella *et al.* (1973)] (0.6 g) in a 33% *w*/*v* solution of methylamine in methanol (15 ml) was heated in a closed vessel at 373 K for 4 h. The excess solvent and amine were removed by distillation under reduced pressure and the resulting residue was suspended in distilled water (40 ml) and stirred for 15 min. The insoluble material (final compound) was collected by filtration, washed with water and recrystallized from the methanol–water (1:2) mixture (yield: 60%; m.p. 456–457 K).

Crystal data

$C_9H_{10}ClN_3O_2S$
$M_r = 259.71$
Monoclinic, $P2_1/a$
$a = 10.096$ (1) Å
$b = 26.316$ (2) Å
$c = 16.927$ (2) Å
$\beta = 90.070$ (2)°
$V = 4497.3$ (8) Å^3
$Z = 16$

$D_x = 1.534$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 219 reflections
$\theta = 2.6$–23.3°
$\mu = 0.51$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.30 × 0.30 × 0.30 mm

Data collection

MAR345 image-plate diffractometer
119 images, 130 mm, $\Delta\Phi$ 3° scans
38 152 measured reflections
6008 independent reflections
4970 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.039$
$\theta_{\max} = 23.3°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 29$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.106$
$S = 1.07$
6008 reflections
598 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0640P)^2 + 0.5031P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0065 (4)

Table 1
Selected geometric parameters (Å, °).

S1A—O1A	1.4322 (16)	S1C—O1C	1.4332 (16)
S1A—O2A	1.4235 (16)	S1C—O2C	1.4173 (16)
S1A—N2A	1.6461 (18)	S1C—N2C	1.6509 (18)
S1A—C10A	1.727 (2)	S1C—C10C	1.731 (2)
N2A—C3A	1.408 (3)	N2C—C3C	1.402 (3)
N2A—C13A	1.470 (3)	N2C—C13C	1.468 (3)
C3A—N4A	1.301 (3)	C3C—N4C	1.307 (3)
C3A—N11A	1.337 (3)	C3C—N11C	1.337 (3)
N4A—C5A	1.390 (3)	N4C—C5C	1.386 (3)
N11A—C12A	1.446 (3)	N11C—C12C	1.444 (3)
S1B—O1B	1.4376 (16)	S1D—O1D	1.4340 (16)
S1B—O2B	1.4233 (15)	S1D—O2D	1.4214 (15)
S1B—N2B	1.6526 (17)	S1D—N2D	1.6508 (17)
S1B—C10B	1.725 (2)	S1D—C10D	1.732 (2)
N2B—C3B	1.405 (2)	N2D—C3D	1.406 (3)
N2B—C13B	1.461 (3)	N2D—C13D	1.464 (3)
C3B—N4B	1.301 (3)	C3D—N4D	1.309 (3)
C3B—N11B	1.336 (3)	C3D—N11D	1.333 (3)
N4B—C5B	1.389 (3)	N4D—C5D	1.386 (3)
N11B—C12B	1.452 (3)	N11D—C12D	1.450 (3)
C3A—N2A—C13A	122.90 (18)	C3C—N2C—C13C	122.90 (18)
C3A—N2A—S1A	116.48 (13)	C3C—N2C—S1C	116.88 (13)
C13A—N2A—S1A	117.70 (15)	C13C—N2C—S1C	116.96 (15)
N4A—C3A—N11A	120.17 (19)	N4C—C3C—N11C	119.81 (19)
N4A—C3A—N2A	123.69 (19)	N4C—C3C—N2C	123.91 (19)
N11A—C3A—N2A	116.09 (17)	N11C—C3C—N2C	116.24 (18)
C3A—N4A—C5A	119.55 (17)	C3C—N4C—C5C	119.69 (18)
C3A—N11A—C12A	122.37 (19)	C3C—N11C—C12C	122.19 (19)
C3B—N2B—C13B	123.56 (17)	C3D—N2D—C13D	122.58 (17)
C3B—N2B—S1B	115.87 (13)	C3D—N2D—S1D	116.17 (13)
C13B—N2B—S1B	117.82 (14)	C13D—N2D—S1D	117.60 (14)
N4B—C3B—N11B	120.46 (19)	N4D—C3D—N11D	120.38 (19)
N4B—C3B—N2B	123.93 (19)	N4D—C3D—N2D	123.45 (19)
N11B—C3B—N2B	115.56 (18)	N11D—C3D—N2D	116.14 (18)
C3B—N4B—C5B	119.71 (17)	C3D—N4D—C5D	119.73 (17)
C3B—N11B—C12B	122.83 (19)	C3D—N11D—C12D	122.86 (19)
S1A—N2A—C3A—N4A	34.6 (3)	S1C—N2C—C3C—N4C	33.6 (3)
C13A—N2A—C3A—N11A	12.2 (3)	C13C—N2C—C3C—N11C	10.1 (3)
N2A—C3A—N4A—C5A	3.4 (3)	N2C—C3C—N4C—C5C	3.5 (3)
N2A—C3A—N11A—C12A	−171.6 (2)	N2C—C3C—N11C—C12C	−171.3 (2)
S1B—N2B—C3B—N4B	35.6 (3)	S1D—N2D—C3D—N4D	36.2 (3)
C13B—N2B—C3B—N11B	13.8 (3)	C13D—N2D—C3D—N11D	12.2 (3)
N2B—C3B—N4B—C5B	2.5 (3)	N2D—C3D—N4D—C5D	2.5 (3)
N2B—C3B—N11B—C12B	−173.1 (2)	N2D—C3D—N11D—C12D	−174.7 (2)

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Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N11A—H11A···O1$B^{\rm i}$	0.78 (2)	2.34 (2)	3.093 (2)	161 (2)
N11B—H11B···O1$A^{\rm ii}$	0.82 (2)	2.27 (2)	3.074 (2)	165 (2)
N11C—H11C···O1$D^{\rm iii}$	0.84 (2)	2.27 (2)	3.058 (2)	157 (2)
N11D—H11D···O1$C^{\rm iv}$	0.86 (2)	2.20 (2)	3.030 (2)	162 (2)

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $-x, 1-y, -z$; (iii) $1-x, 1-y, 1-z$; (iv) $-x, 1-y, 1-z$.

The diffraction data are limited because of a rather poor quality crystal. The data collection was stopped when the $R_{\rm int}$ of the equivalent reflections became too high. All H atoms [with the exception of the nitrogen-bound atoms H11(A–D)] were included in the refinement in the riding model approximation with isotropic displacement parameters fixed at $1.2U_{\rm eq}$ of the parent atom ($1.5U_{\rm eq}$ for methyl H atoms). The H11(A–D) atoms were refined isotropically (their displacement parameters being fixed at $1.2U_{\rm eq}$ of the corresponding nitrogen atom). The N—H distances are in the range 0.78–0.86 Å. Even though their geometrical similarity and particular relative disposition suggest that the crystallographically independent molecules are pairwise related by the local symmetry elements, a thorough check for additional genuine crystal symmetry yielded no result.

Data collection: MAR software; cell refinement: *marHKL* (Klein & Bartels, 2000); data reduction: *marHKL*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

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