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7-Amino-3-methyl-4*H*-imidazo[2,3-*c*][1,2,6]thiadiazine 5,5-Dioxide

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Abstract. $C_5H_7N_5O_2S$, monoclinic, space group $P2_1/c$, $a = 10{\cdot}168\ (1)$, $b = 8{\cdot}734\ (1)$, $c = 9{\cdot}460\ (1)$ Å, $\beta = 103{\cdot}71\ (1)°$, $V = 816{\cdot}2\ (3)$ Å^3, $Z = 4$, $M_r = 201{\cdot}2$, $D_x = 1{\cdot}64$ g cm^{-3}. The structure has been determined by standard Fourier techniques from X-ray diffractometer data and refined by least-squares methods to $R = 0{\cdot}097$ for the 662 observed reflexions. Hydrogen bonding is present. A half-normal probability comparison with other thiadiazine derivatives has been made.

Introduction. A crystal 0·21 × 0·20 × 0·22 mm was chosen for data collection. Intensity measurements were recorded on a Philips PW 1100 four-circle diffractometer. A θ–2θ scan, with graphite-monochromated Mo $K\alpha$ radiation, was used to measure 1065 independent reflexions; of these, 662 were considered as observed by the criterion $I > 2\sigma(I)$ (σ from counting statistics). The intensity data were reduced to structure factors by the application of Lorentz and polarization factors, but no correction for absorption was applied.

The location of the heavy atom was determined by the three-dimensional Patterson method. The refinement was carried out by full-matrix least-squares techniques. All H atoms were revealed on a difference map. The weighting scheme at this stage was $w = K/[f(F_o)]^2f(S)$ where $f(S) = 5{\cdot}65 - 24{\cdot}25S + 29{\cdot}35S^2$ with $S = \sin\theta/\lambda$, $f(F_o) = -0{\cdot}37 + 0{\cdot}78F_o - 0{\cdot}08F_o^2$ for $F_o < 7{\cdot}0$ and $f(F_o) = 1{\cdot}41 - 0{\cdot}05F_o$

Table 1. *Final atomic coordinates*

	x	*y*	*z*
N(1)	0·6349 (10)	0·2953 (10)	0·4516 (9)
C(2)	0·7099 (12)	0·2518 (13)	0·5765 (11)
N(3)	0·7888 (9)	0·3641 (9)	0·6528 (8)
N(4)	0·8095 (10)	0·6373 (10)	0·6060 (8)
S(5)	0·7747 (3)	0·7601 (3)	0·4708 (2)
N(6)	0·6365 (11)	0·7126 (10)	0·3634 (10)
C(7)	0·5992 (13)	0·5642 (12)	0·3458 (11)
C(8)	0·6654 (13)	0·4540 (12)	0·4472 (10)
C(9)	0·7560 (11)	0·4913 (11)	0·5704 (9)
N(10)	0·4986 (12)	0·5300 (10)	0·2353 (10)
C(11)	0·8872 (13)	0·3516 (12)	0·7937 (11)
O(*a*)	0·8814 (8)	0·7494 (11)	0·3932 (8)
O(*b*)	0·7605 (11)	0·9062 (9)	0·5341 (8)
H(2)	0·717 (15)	0·157 (21)	0·595 (17)
H(4)	0·859 (15)	0·692 (20)	0·708 (17)
H(10*a*)	0·450 (15)	0·607 (21)	0·162 (16)
H(10*b*)	0·459 (15)	0·444 (20)	0·221 (16)
H(11*a*)	0·984 (14)	0·382 (20)	0·791 (17)
H(11*b*)	0·898 (16)	0·267 (20)	0·813 (17)
H(11*c*)	0·850 (15)	0·414 (21)	0·873 (17)

Table 2. *Molecular geometry*

(*a*) Bond distances (Å) and angles (°)

N(1)–C(2)	1·30 (1)	S(5)–O(*a*)	1·45 (1)
C(2)–N(3)	1·36 (1)	S(5)–O(*b*)	1·43 (1)
N(3)–C(9)	1·35 (1)	N(6)–C(7)	1·35 (1)
N(3)–C(11)	1·47 (1)	C(7)–C(8)	1·41 (1)
N(4)–S(5)	1·64 (1)	C(7)–N(10)	1·31 (1)
N(4)–C(9)	1·40 (1)	C(8)–N(1)	1·42 (1)
S(5)–N(6)	1·58 (1)	C(8)–C(9)	1·34 (1)
C(8)–N(1)–C(2)	103·1 (8)	O(*a*)–S(5)–O(*b*)	115·5 (6)
N(1)–C(2)–N(3)	114·6 (10)	S(5)–N(6)–C(7)	120·8 (8)
C(2)–N(3)–C(9)	104·7 (8)	N(6)–C(7)–C(8)	119·8 (9)
C(2)–N(3)–C(11)	128·1 (9)	N(6)–C(7)–N(10)	117·4 (9)
C(9)–N(3)–C(11)	127·3 (8)	C(8)–C(7)–N(10)	122·8 (10)
S(5)–N(4)–C(9)	114·1 (6)	N(1)–C(8)–C(7)	127·8 (9)
N(4)–S(5)–N(6)	108·9 (5)	N(1)–C(8)–C(9)	108·7 (8)
N(4)–S(5)–O(*a*)	107·7 (5)	C(7)–C(8)–C(9)	122·8 (9)
N(4)–S(5)–O(*b*)	106·3 (5)	N(3)–C(9)–N(4)	125·6 (8)
N(6)–S(5)–O(*a*)	108·4 (5)	N(3)–C(9)–C(8)	109·0 (9)
N(6)–S(5)–O(*b*)	109·9 (6)	N(4)–C(9)–C(8)	125·4 (9)

(*b*) Main least-squares planes in the molecule with their dihedral angle. An asterisk denotes the atoms used in the plane calculations. Atomic deviations are in Å.

	Plane 1	Plane 2		Plane 1	Plane 2
N(1)	−0·059	0·004*	N(6)	0·002*	−0·221
C(2)	−0·168	−0·011*	C(7)	−0·018*	−0·168
N(3)	−0·125	0·014*	C(8)	0·034*	0·005*
N(4)	0·014*	−0·027	C(9)	−0·032*	−0·012*
S(5)	0·439	0·258	N(10)	−0·126	−0·323
O(*a*)	1·884	1·691	C(11)	−0·176	0·050
O(*b*)	−0·283	−0·523			

∠(Plane 1) (Plane 2) 5·0°

(*c*) Torsional angles

N(4)–S(5)–N(6)–C(7)	−31 (1)°
S(5)–N(6)–C(7)–C(8)	15 (2)
N(6)–C(7)–C(8)–C(9)	7 (2)
C(7)–C(8)–C(9)–N(4)	−9 (2)
C(8)–C(9)–N(4)–S(5)	−11 (2)
C(9)–N(4)–S(5)–N(6)	28 (1)

otherwise, and $K = 0{\cdot}61$. A final least-squares refinement with this weighting scheme was performed. The weighted and unweighted agreement indices for the observed reflexions were 0·111 and 0·097 respectively $[R_w = (\Sigma\, w\Delta^2/\Sigma\, w|F_o|^2)^{1/2}]$, with no trends in $\langle w\Delta^2\rangle$. The final difference synthesis showed two peaks of 1·1 and 0·8 e Å^{-3} in the vicinity of the S atom, but neither chemical significance nor any model of disorder could be attributed to them (Cook & Bugg, 1976; Koch, De Ranter, Rolies & Dideberg, 1976). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).*

Discussion. The fractional atomic coordinates are given in Table 1. Table 2 shows bond distances and angles for the heavy atoms using the numbering system given in Fig. 1, together with the main planes of the molecule and the torsional angles. The average C—H and N—H bond lengths are 0·92 and 0·98 Å respectively. The molecule has two close contacts (N—H···O and N—H···N) of 2·82 and 3·03 Å respectively. The N—H···*Y* angles are 157·1 and 168·1°.

A half-normal probability analysis (Fig. 2) has been used to compare the intramolecular distances of the

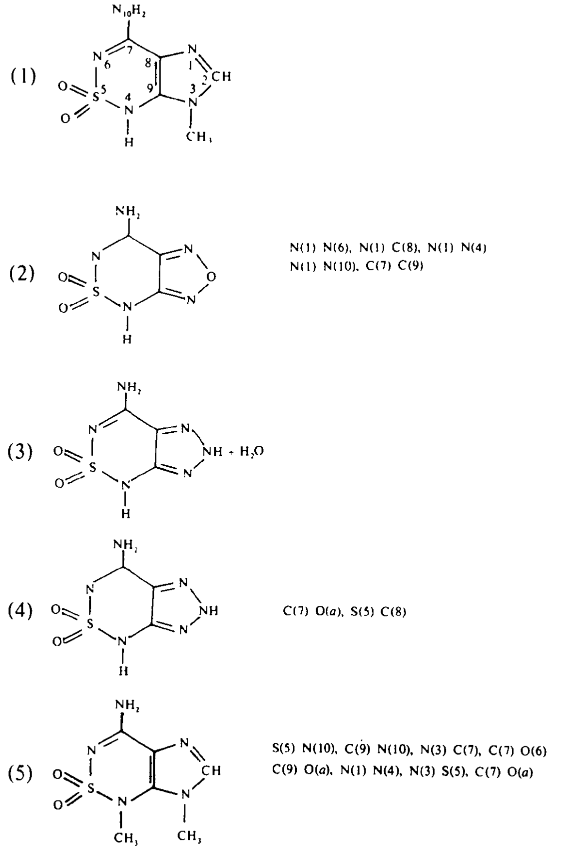

Fig. 2. Schematic drawing of the molecules compared by half-normal probability methods. (1) is the title compound.

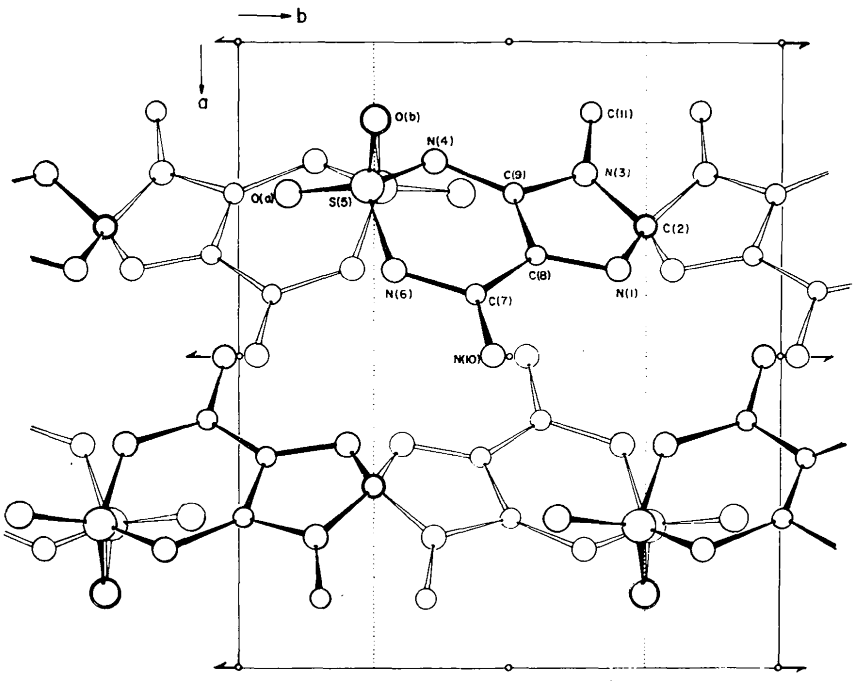

Fig. 1. A projection of the structure along [001].

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32862 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

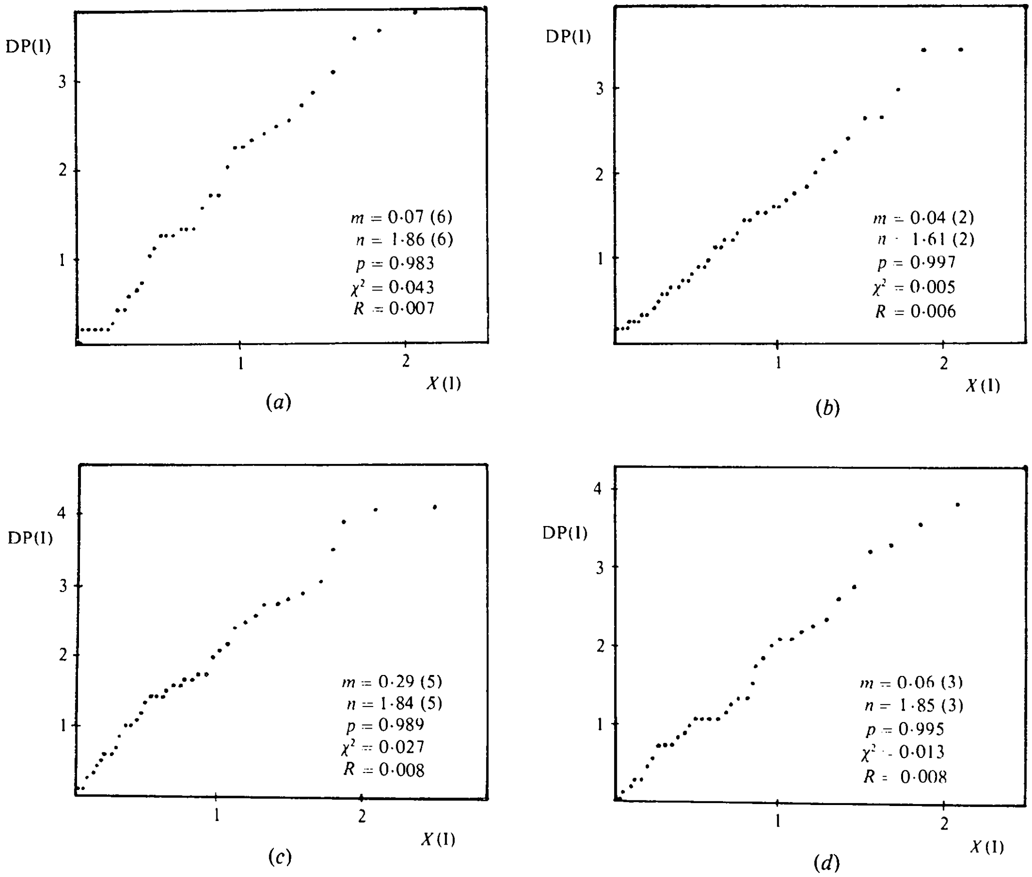

Fig. 3. Half-normal probability plots for intramolecular distances. Comparisons were made of the title compound (1) with (*a*) compound 2, (*b*) compound 3, (*c*) compound 4, (*d*) compound 5 (see Fig. 2).

present compound with those of similar compounds already studied (Foces-Foces, Cano, García-Blanco & Rodríguez, 1975; Foces-Foces, Cano & García-Blanco, 1975*a*,*b*; Smith-Verdier, Florencio, García-Blanco & Rodríguez, 1977). From these plots the parameters which give systematic departures were eliminated until straight lines with slopes approximating the supposed underestimation of the e.s.d.'s (Abrahams & Keve, 1971) were obtained (Fig. 3). For these, ρ and χ^2 $\{\rho = \mu_{11}/\sigma_x\sigma_y,\ \chi^2 = \sigma_y^2(1-\rho^2),\ \sigma_x = [(S_x)^2/N - S_x/N^2]^{1/2},\ \mu_{11} = S_{xy}/N - S_xS_y/N^2\}$ have been calculated (Fig. 3). In this way we have obtained the pairs of parameters, shown in Fig. 2, giving the systematic deviations. The biggest differences were found between compound 5 and the title compound, while compound 3 is the one most similar to the present compound. The bias in the parameters could be interpreted in terms of (*a*) the angle between the OSO and NSN planes, 89·6, 89·1, 89·0, 89·3 and *80·6*° respectively for compounds 1 to 5, (*b*) the torsional angles C(3)–C(9)–C(8)–C(7) and C(1)–C(8)–C(9)–C(4), which have values of 172·5, 178·4, 178·1, 178·4, *175·9*° and −179·4, −177·8, −176·6, −177·3 and *178·3*° respectively, and (*c*) the N(1)–C(8) distance with values of 1·423, 1·299, 1·346, 1·338 and 1·391 Å. We think that these are the main causes of distortion of the thiadiazine skeleton.

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Remeasurement of Optically Active $NaClO_3$ and $NaBrO_3$

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Abstract. $NaClO_3$, $NaBrO_3$, both cubic, space group $P2_13$, a = 6·57584 (5) and 6·70717 (10) Å respectively, corrected to 298·2 K, for $\lambda(\mathrm{Cu}\ K\alpha_1) = 1\cdot540598$ Å; $Z = 4$, $D_m = 2\cdot49\ (1)$, $D_x = 2\cdot486$ g cm^{-3} for $NaClO_3$ and $D_m = 3\cdot34\ (2)$, $D_x = 3\cdot321$ g cm^{-3} for $NaBrO_3$. The study crystals, grown from aqueous solution by K. Nassau with 99·9% pure starting material, are shown by anomalous scattering measurements to possess the same chirality. Least-squares refinement resulted in $R = 0\cdot013$ for 671 ($NaClO_3$), and $R = 0\cdot034$ for 489 ($NaBrO_3$) structure factors. The Cl and Br atoms occupy distorted octahedra. Three Cl–O bonds are 1·485 (1) Å, and three others are 3·086 (1) Å. The corresponding Br–O bond lengths are 1·648 (4) and 2·974 (4) Å.

Introduction. The crystal structure of $NaClO_3$ was first determined by Zachariasen (1929) and was subsequently redetermined by Ramachandran & Chandrasekaran (1957), Aravindakshan (1959), Bower, Sparks & Trueblood (1959) and Zachariasen (1965). The crystal structure of $NaBrO_3$ was first determined by Dickinson & Goodhue (1921) and Kolkmeijer, Bijvoet & Karssen (1923) and was subsequently redetermined by Hamilton (1938) and Beurskens-Kerssen, Kroon, Endeman, Van Laar & Bijvoet (1963). Crystals of the two materials are isomorphous, in the enantiomorphous point group 23. The present interest in a complete remeasurement of the two crystal structures lies in redetermining the relationship between the chirality and the optical activity of each crystal (*cf.* Beurskens-Kerssen *et al.*, 1963; Chandrasekaran & Mohanlal, 1976). The earlier sets of atomic coordinates are collected in Table 1.

The lattice constants of $NaClO_3$ and $NaBrO_3$ were measured at 295 K, and corrected to 298·2 K, on a modified (Barns, 1967) version of Bond's (1960) precision lattice constant diffractometer, based on $\lambda(\mathrm{Cu}\ K\alpha_1) = 1\cdot540598$ Å. A single crystal of $NaClO_3$, ground to a sphere with diameter 0·299 (8) mm, $\mu R = 0\cdot190$, was mounted in random orientation on a Pyrex capillary. The intensities of all reflections in a sphere with reciprocal lattice radius $(\sin\theta)/\lambda = 0\cdot99$ Å^{-1} and with $-12 \leq h, k, l \leq +12$ were measured on a CAD-4 diffractometer controlled by a PDP 8e computer with standard Enraf–Nonius programs. The radiation used was Nb-filtered Mo $K\alpha$. The Laue symmetry is $m3$ and the only systematic absences are $h00$ for $h = 2n + 1$, and cyclic interchange: the space group of this optically active crystal is hence $P2_13$.

7533 reflections were measured, including some duplicates and a group of four standards that followed

Table 1. *Atomic coordinates reported in the literature for* $NaClO_3$ *and for* $NaBrO_3$

x (Na)	x (Cl)	x (Br)	x (O)	y (O)	z (O)	Reference
0·064	0·417	–	0·303	0·592	0·500	Zachariasen (1929)
0·066 (1)	0·418 (1)	–	0·307 (2)	0·594 (2)	0·508 (2)	Aravindakshan (1959)
0·066 (3)	0·417 (2)	–	0·305 (2)	0·592 (2)	0·494 (2)	Bower *et al.* (1959)
0·0685 (5)	0·4186 (3)	–	0·3033 (7)	0·5938 (8)	0·5065 (9)	Zachariasen (1965)
0·09	–	0·41	0·30	0·60	0·47	Dickinson & Goodhue (1921)
0·083	–	0·417	0·306	0·50	0·417	Kolkmeijer *et al.* (1923)
0·075 (3)	–	0·405 (2)	0·258 (6)	0·614 (6)	0·480 (6)	Hamilton (1938)
0·077	–	0·4063	0·287	0·597	0·508	Beurskens-Kerssen *et al.* (1963)