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The Crystal Structure of 7-Amino-2*H*,4*H*-*vic*-triazolo[4,5-*c*]-1,2,6-thiadiazine-1,1-dioxide (ATT)

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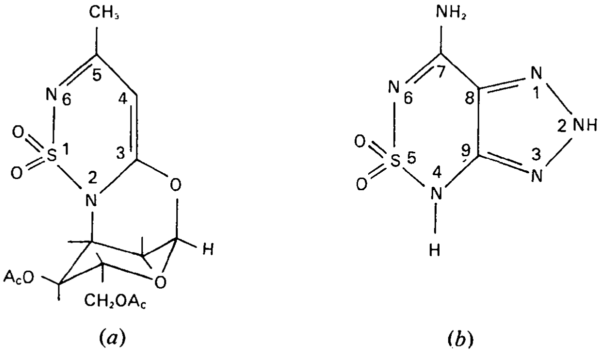
The structure of $C_3H_4N_6O_2S$ (ATT) has been determined by single-crystal X-ray analysis from diffractometer data, and has been refined by least-squares calculations to an R of 0·043 for 1191 observed reflexions. Crystals are orthorhombic, *Pbca*, with $a=13{\cdot}552$ (2), $b=14{\cdot}405$ (3), $c=6{\cdot}485$ (1) Å, $D_{obs}=1{\cdot}98$, $D_{cal}=1{\cdot}97$ g cm^{-3}, $Z=8$, $V=1272{\cdot}6$ Å^3. The molecular geometry shows distortions of S–N valence distances, which are slightly shorter than might be expected for single-bond distances. The thiadiazine ring has an envelope conformation at the sulphur atom. The molecules are linked together by a plausible system of hydrogen bonds.

Introduction

A series of compounds has been synthesized by García Muñoz and M. Stud (personal communication) in order to study the N–SO$_2$–N group (which has a volume similar to that of the N–CO–N group) in heterocyclic systems. The crystal structures of two such compounds, $C_{14}H_{18}N_2O_8S$ (TDR) and $C_3H_4N_6O_2S$ (ATT), have been solved by X-ray diffraction techniques. The former (Foces-Foces, Smith, Florencio & García-Blanco, 1975) has the structure shown in Fig. 1(*a*). The latter [Fig. 1(*b*)], has now been investigated to obtain more information about the thiadiazine ring. This should give a better understanding of the behaviour of these compounds in substitution reactions. Another purpose of this work was to establish the hydrogen position on the five-membered ring, which could not be determined by other techniques.

Experimental

Suitable single crystals of ATT were kindly supplied by García Muñoz and M. Stud (Instituto Química Organica General, CSIC, Madrid). Crystal data are listed in Table 1. The density was measured in a mixture of benzene and methylene iodide. X-ray intensities were obtained on an automatic Philips PW 1100 diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. A crystal with dimensions $0{\cdot}2\times0{\cdot}2\times0{\cdot}1$ mm was used for collecting 1824 independent reflexions between 2 and 30° in θ (using the $\omega/2\theta$ scan mode). Of these 633 reflexions were considered unobserved by the criterion I unobserved if $I<2\sigma(I)$, with $I=C_p-C_b$ and $\sigma^2(I)=C_p+C_b+(0{\cdot}04)^2I^2$, where C_p and C_b are peak counts and background respectively.



(*a*) (*b*)

Fig. 1. (*a*) TDR. (*b*) ATT.

Table 1. *Crystal data*

Standard deviations, given in parentheses, refer to the least significant digits.

Molecular formula	$C_3H_4N_6O_2S$
M.W.	188·06
System	Orthorhombic
Space group	*Pbca*
Wavelength (Mo $K\bar{\alpha}$)	0·7107 Å
a	13·552 (2) Å
b	14·405 (3)
c	6·485 (1)
Z	8
V	1272·6 Å^3
D_{obs}(flotation)	1·98 g cm^{-3}
D_{cal}	1·97 g cm^{-3}
F_{000}	760
μ	4·654 cm^{-1}

Structure determination and refinement

Corrections were applied for Lorentz and polarization effects but not for absorption. All non-hydrogen atoms were located on an E map with the phases of 261 E's $\geq$ 1·5, which were calculated by the multisolution tangent formula program *MULTAN* (Main, Woolfson & Germain, 1971). After six cycles of full-matrix least-squares refinement for the 1191 observed reflexions with isotropic temperature factors and two more cycles with anisotropic temperature factors, the conventional R value for the observed reflexions was 0·055.

All hydrogen-atom positions were determined from a difference Fourier map. The hydrogen atom in the

Table 2. *Coefficients for the weighting echeme*

	a	*b*		*c*	*d*
$\lvert F_o\rvert \leq 5{\cdot}59$	1·80	0·0	$\sin\theta < 0{\cdot}56$	3·48	−3·79
$5{\cdot}59 < \lvert F_o\rvert \leq 15{\cdot}55$	1·82	−0·04	$0{\cdot}56 \leq \sin\theta < 0{\cdot}75$	1·31	0·01
$15{\cdot}55 < \lvert F_o\rvert \leq 32{\cdot}05$	1·21	−0·00	$0{\cdot}75 \leq \sin\theta$	−0·26	1·96
$32{\cdot}05 < \lvert F_o\rvert$	−0·76	0·05			

five-membered ring was found to be bonded to the N(2) nitrogen atom. The refinement was continued including these atoms with a fixed isotropic temperature factor equivalent to the anisotropic temperature factors of the atoms to which the hydrogen atoms are bonded (Hamilton, 1959).

An examination of the $\langle w\Delta^2\rangle$ ($\Delta = F_o - F_c$) values as a function of $\lvert F_o\rvert$ and $\sin\theta$ suggested that the best weighting scheme was $w = w_1 . w_2$ where $w_1 = 1/\sigma_1^2$ and $w_2 = 1/\sigma_2^2$ with $\sigma_1 = a + b\lvert F_o\rvert$ and $\sigma_2 = c + d . \sin\theta$ with the coefficients given in Table 2.

After least-squares refinement with these weights, the final unweighted and weighted agreement indices were $R = 0{\cdot}048$ and $R_w = 0{\cdot}043$, where $R_w = (\sum w\Delta^2/\sum w\lvert F_o\rvert^2)^{1/2}$. A final difference synthesis had no electron density greater than 0·34 e Å^{-3}. The values of the coordinates of all atoms and the thermal parameters of the non-hydrogen atoms, both with standard deviations, are given in Tables 3 and 4.*

The atomic scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962).

The molecular structure

The two least-squares ring planes in the molecule are shown in Table 5 referred to an orthonormal system parallel to the crystallographic one. It can be seen that the six-membered ring (plane 1), excluding the sulphur atom, is almost planar, the sulphur atom being 0·3 Å out of the plane while the average deviation of the remaining atoms is 0·008 Å. The torsional angles (Klyne & Prelog, 1960) in the thiadiazine ring are given in Table 6. The six-membered ring has an envelope conformation at the sulphur atom.

Table 3. *Final fractional atomic coordinates* (× 10^4) *for all independent atoms*

	x	*y*	*z*
N(1)	3603 (2)	2518 (2)	4079 (5)
N(2)	3266 (2)	3378 (2)	4210 (5)
N(3)	2283 (2)	3476 (2)	4485 (5)
N(4)	1027 (2)	2306 (2)	4889 (5)
S(5)	785 (1)	1187 (1)	4487 (2)
O(5*a*)	379 (2)	1113 (2)	2439 (5)
O(5*b*)	156 (2)	910 (2)	6150 (5)
N(6)	1791 (2)	630 (2)	4611 (6)
C(7)	2680 (2)	1001 (2)	4350 (6)
C(8)	2787 (2)	2005 (2)	4298 (6)
C(9)	1979 (2)	2598 (2)	4543 (5)
N(10)	3467 (2)	462 (2)	4261 (6)
H(2)	3664 (35)	3887 (34)	4368 (85)
H(4)	542 (33)	2676 (32)	5508 (90)
H(10*a*)	3340 (37)	−161 (34)	4345 (95)
H(10*b*)	4052 (36)	732 (35)	4049 (93)

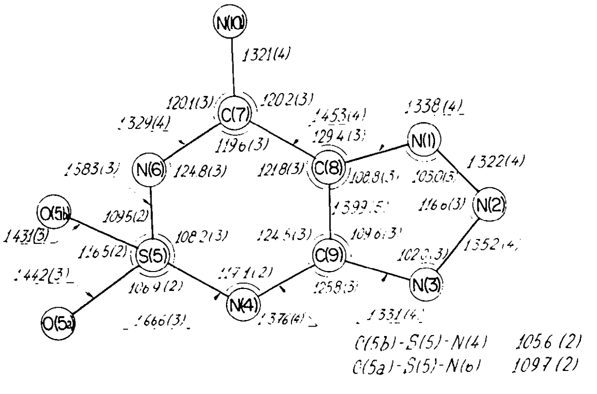


Fig. 2. Bond lengths (Å), valence angles (°), and their estimated standard deviations referred to the least significant digits.

Table 4. *Thermal parameters* (× 10^4) *for the heavy atoms as defined in the expression exp* $(-2\pi^2\sum U_{ij}a_i^*a_j^*h_ih_j)$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{iso}
N(1)	208 (15)	155 (14)	291 (18)	−8 (13)	−11 (14)	3 (13)	1·72 (12)
N(2)	179 (15)	149 (15)	345 (19)	−20 (12)	−22 (15)	11 (14)	1·77 (12)
N(3)	208 (16)	132 (14)	329 (18)	−8 (12)	−22 (15)	−5 (14)	1·76 (12)
N(4)	159 (15)	130 (15)	427 (21)	−11 (12)	22 (14)	−1 (14)	1·89 (13)
S(5)	118 (4)	126 (4)	318 (5)	−9 (3)	−3 (4)	17 (4)	1·48 (3)
O(5*a*)	244 (15)	220 (13)	437 (17)	−39 (12)	−120 (13)	15 (14)	2·37 (12)
O(5*b*)	224 (15)	221 (14)	483 (20)	12 (12)	114 (14)	74 (14)	2·44 (13)
N(6)	132 (14)	133 (14)	397 (20)	−1 (12)	8 (15)	1 (15)	1·74 (13)
C(7)	183 (17)	172 (16)	211 (17)	4 (14)	0 (15)	23 (15)	1·49 (13)
C(8)	160 (17)	171 (16)	245 (19)	−22 (14)	−4 (15)	12 (16)	1·52 (14)
C(9)	165 (16)	158 (16)	231 (18)	5 (14)	−16 (16)	−9 (15)	1·46 (13)
N(10)	145 (15)	195 (16)	500 (24)	46 (13)	48 (17)	−17 (17)	2·21 (15)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30878 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. *Deviations of some atoms from the best two ring planes of the molecule*

Atoms used in the plane calculations are asterisked.

Plane 1		Plane 2	
	d (Å)		*d* (Å)
N(4)	0·010*	N(1)	−0·002*
S(5)	−0·300	N(2)	0·002*
O(5*a*)	−1·700	N(3)	−0·001*
O(5*b*)	0·634	C(8)	0·001*
N(6)	−0·010*	C(9)	0·000*
C(7)	0·010*		
C(8)	0·000*		
C(9)	−0·011*		
N(10)	0·117		

Plane 1: $0·1549X+0·0010Y+0·9879Z+3·3471=0·0$
Plane 2: $0·1339X-0·0148Y+0·9909Z+3·2293=0·0$
Angle (Plane 1)/(Plane 2) = 1·53°

Table 6. *Twist angles*

S(5)–N(6)–C(7)–C(8)	11·32°
C(8)–C(9)–N(4)–S(5)	−13·66
N(6)–C(7)–C(8)–C(9)	0·91
C(7)–C(8)–C(9)–N(4)	−1·21
C(9)–N(4)–S(5)–N(6)	21·50
N(4)–S(5)–N(6)–C(7)	−21·42

The interatomic distances and angles are shown in Fig. 2. Although the thiadiazine ring exhibits analogous characteristics in TDR and ATT, there appear to be three major differences: (*a*) the S–O distances in TDR were different [1·451 (7), 1·426 (8) Å] while here they are alike; (*b*) in the TDR compound the O(1*b*) oxygen atom was almost in the thiadiazine plane (0·049 Å) while here O(5*b*) is 0·634 Å out the plane; (*c*) there exist some differences between the S–N distances [1·583 (3) and 1·666 (3) Å in ATT *versus* 1·598 (9) and 1·712 (8) Å in TDR]. The long distance of 1·712 Å in TDR could be explained by interactions between O(1*b*) of the base and the sugar, while in ATT there are no such interactions. Nevertheless the values of 1·583 and 1·598 Å are shorter than might be expected for a single-bond distance.

All C–N and N–N distances in the five-membered ring are longer than the corresponding double bonds and much shorter than the single bonds (Sabesan & Venkatesan, 1971). The short C(7)–N(10) bond is similar to the exocyclic C–N bonds found in pyrimidine and purine systems (Watson, Sutor & Tollin, 1965).

Geometry of the hydrogen bonds

The packing in the crystal is due to van der Waals forces and weak hydrogen interactions. Atomic distances and angles of interest for the characterization of the hydrogen bonds are given in Table 7. Each molecule is linked to four molecules by contacts of the types N···O and N···N equal to or smaller than 3·0 Å. H(10*a*) and H(10*b*) do not deviate significantly from plane 1 (Table 5). The suggested hydrogen bonds are marked with asterisks in Table 7 (Hamilton & Ibers, 1968; Donohue, 1968; Hamilton, 1968).

Table 7. *Hydrogen bonds, short* X–H···Y *van der Waals contacts and group features*

X_a, X'_a, Y_a, Y'_a are the atoms bonded to X and Y respectively; distances are in Å and angles in degrees, with e.s.d.'s in parentheses.

Atoms

X'_a	X_a	X	H	Y	Y_a	Y'_a
N(3)	N(1)	N(2)	H(2)	N(6) (*L*)	S(5) (*L*)	C(7) (*L*)
N(3)	N(1)	N(2)	H(2)	O(5*b*) (*K*)	S(5) (*K*)	
S(5)	C(9)	N(4)	H(4)	N(1) (*D*)	N(2) (*D*)	C(8) (*D*)
S(5)	C(9)	N(4)	H(4)	O(5*a*) (*C*)	S(5) (*C*)	
	C(7)	N(10)	H(10*a*)	N(3) (*H*)	N(2) (*H*)	C(9) (*H*)
	C(7)	N(10)	H(10*b*)	O(5*a*) (*F*)	S(5) (*F*)	

X···Y	X–H	H···Y	X–H···Y	H–X···Y
3·261 (4)	0·918 (49)	2·594 (49)	130·1 (40)	37·5 (32)
2·774 (4)	0·918 (49)	2·075 (48)*	132·0 (42)	33·8 (32)
3·368 (4)	0·940 (48)	2·661 (45)	132·5 (38)	35·6 (30)
2·954 (4)	0·940 (48)	2·161 (50)*	141·4 (42)	27·2 (30)
3·044 (4)	0·917 (49)	2·142 (49)*	167·6 (48)	8·7 (34)
2·973 (4)	0·895 (49)	2·117 (52)*	159·7 (48)	14·3 (34)

Symmetry code

(*C*)	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	(*H*)	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	z
(*D*)	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$	(*K*)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$
(*F*)	$\frac{1}{2}+x$	y	$\frac{1}{2}-z$	(*L*)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	z

Description of the thermal motion

The magnitudes and directions of the principal axes of thermal vibration have been calculated from the anisotropic temperature parameters. In general the maximum r.m.s. displacements for all atoms are along the **c** direction. Thus the molecules, linked by hydrogen bonds, exhibit maximum vibration essentially perpendicular to their plane.

All the calculations were performed with programs of the X-RAY 70 System running on the 1108 UNIVAC computer of the Centro de Proceso de Datos del Ministerio de Educación y Ciencia (Madrid).

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