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The Crystal Structure of 7-Amino-4*H*-furazo[3,4-*d*]-1,2,6-thiadiazine-1,1-dioxide

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The single-crystal structure of $C_3H_3N_5O_3S$ was determined by a three-dimensional X-ray study. It crystallizes in the space group $P2_1/c$ with cell dimensions $a=9{\cdot}901$ (1), $b=4{\cdot}992$ (1), $c=13{\cdot}852$ (1) Å and $\beta=108{\cdot}53$ (1)°. The structure was solved with the Patterson function. Full-matrix least-squares treatment gave a final unweighted R value of 0·035. The thiadiazine ring conformation in the molecule was found in the expected envelope form at the sulphur atom. An interpretation of experimental results is given in terms of molecular diagrams. The molecules are linked by van der Waals forces and N–H···O and N–H···N weak hydrogen interactions.

Introduction

This study has been carried out as part of a research programme on new heterocyclic systems with the $N–SO_2–N$ group. These compounds have been prepared by Drs García-Muñoz and Stud (Itt°. Química Orgánica Médica, CSIC, Madrid) in order to obtain substances with biological activity. The crystal structures of several molecules containing this group have recently been reported (Foces-Foces, Cano & García-Blanco, 1975*a*,*b*). The purpose of the present paper is to report the X-ray structure determination of 7-amino-4*H*-furazo[3,4-*d*]-1,2,6-thiadiazine-1,1-dioxide and discuss the main features involving the bond lengths found in the thiadiazine ring.

Experimental

A quasi-spherical single crystal of dimensions $0{\cdot}3\times0{\cdot}3\times0{\cdot}3$ mm was selected for X-ray investigation. Its density was determined in a mixture of benzene and methylene iodide. The lattice constants were obtained from a least-squares analysis of the settings of 19 reflexions measured on a four-circle diffractometer with Mo $K\alpha$ radiation monochromatized by graphite.

Crystal data

The crystals are monoclinic, space group $P2_1/c$. $C_3H_3N_5O_3S$, $M=189{\cdot}1$, $a=9{\cdot}901$ (1), $b=4{\cdot}992$ (1), $c=13{\cdot}852$ (1) Å, $\beta=108{\cdot}53$ (1)°; $V=649{\cdot}1$ Å^3, $Z=4$, $d_m=2{\cdot}00$, $d_c=1{\cdot}93$ g cm^{-3}, $F(000)=384$, Mo $K\alpha$ radiation, $\lambda=0{\cdot}7107$ Å, $\mu=4{\cdot}85$ cm^{-1}.

The intensities were collected on a Philips PW1100 four-circle diffractometer operating in the $\omega/2\theta$ scan mode. 2843 reflexions up to $\theta=35°$ were measured. 397 were considered unobserved by the criterion $I<2\sigma(I)$ where $I=C_p-C_b$ (C_p and C_b are peak counts and background counts respectively) and $\sigma^2(I)=C_p+C_b+(0{\cdot}04)^2I^2$.

During the data collection three standard reflexions were measured every 90 min to check the stability of crystal and electronics. All the values obtained for these reflexions were treated graphically and the average values of the fluctuations turned out to be less than 7%. The data were corrected for Lorentz and polarization effects, but not for absorption. An overall temperature factor ($B=1{\cdot}82$ Å^2) and scale factor were evaluated from a Wilson plot and used at the beginning of this study.

Solution and refinement of the structure

The position of the sulphur atom was determined from a Patterson map. Further Fourier analysis located all remaining atoms in the molecule. The R value was 0·28. The structure was refined by full-matrix least-squares methods and the R value was reduced to 0·046. The hydrogen atoms were located in a difference synthesis. These atoms were subsequently included in the refinement with isotropic temperature factors equivalent to the anisotropic temperature factors of the atoms to which hydrogens are bonded (Hamilton, 1959).

The weighting scheme was $w=w_1\,.\,w_2$ where $w_1=1/\sigma_1^2$ and $w_2=1/\sigma_2^2$ with $\sigma_1=0{\cdot}43-0{\cdot}03|F_o|$ when $|F_o|\le10{\cdot}0$ and $\sigma_1=-0{\cdot}13+0{\cdot}04|F_o|$ when $10{\cdot}0<|F_o|$ and $\sqrt{\sigma_2}=0{\cdot}67/\sin\theta$. After least-squares refinement this scheme gave average values of $w\Delta^2$ ($\Delta=F_o-F_c$) for groups of reflexions independent of the values of $\sin\theta$ and $|F_o|$. The final unweighted and weighted agreement indices for the observed reflexions were $R=0{\cdot}035$ and $R_w=0{\cdot}043$ respectively, where $R_w=(\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$. The ratio of maximum shift to the error for the heavy atoms in the last cycle of refinement was 0·03, and the average value was 0·01. The residual electron density did not exceed 0·35 e Å^{-3}.

The positional coordinates and thermal parameters, together with their standard deviations, are listed in

Tables 1 and 2. The bond distances and angles are collected in Fig. 1. Atomic scattering factors were taken from *International Tables for X-ray Crystallography*.*

Table 1. *Final atomic coordinates*

The least-squares e.s.d.'s given in parentheses affect the last digits.

	x	y	z
N(1)	0·31515 (12)	0·46661 (23)	0·20198 (8)
O(2)	0·42220 (11)	0·61905 (21)	0·26428 (8)
N(3)	0·45705 (11)	0·53674 (22)	0·36648 (8)
N(4)	0·36345 (11)	0·17829 (23)	0·44171 (7)
S(5)	0·21476 (3)	−0·00185 (5)	0·42404 (2)
O(5*a*)	0·25786 (13)	−0·24300 (19)	0·47991 (8)
O(5*b*)	0·11434 (10)	0·16025 (21)	0·45308 (7)
N(6)	0·15476 (12)	−0·06690 (24)	0·30551 (7)
C(7)	0·17677 (11)	0·08226 (23)	0·23361 (7)
C(8)	0·28205 (11)	0·29620 (22)	0·26167 (7)
C(9)	0·37004 (10)	0·33767 (22)	0·36349 (7)
N(10)	0·11062 (14)	0·03646 (29)	0·13676 (7)
H(4)	0·40166 (297)	0·21336 (571)	0·50424 (224)
H(10*a*)	0·04576 (296)	−0·09590 (656)	0·11933 (219)
H(10*b*)	0·13524 (257)	0·12378 (489)	0·09182 (195)

Table 2. *Thermal parameters for the heavy atoms, given according to the expression exp* $(-2\pi^2\sum U_{ij}a_i^*a_j^*h_ih_j)$

The hydrogen thermal parameters are the equivalent isotropic temperature factors of the corresponding heavy atoms. The least-squares e.s.d.'s are given in parentheses affecting the last digits.

	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}
S(5)	296 (1)	205 (1)	171 (1)	14 (1)	80 (1)	6 (1)
O(5*a*)	595 (6)	245 (4)	305 (4)	70 (4)	163 (4)	65 (3)
O(5*b*)	350 (4)	387 (5)	301 (4)	94 (4)	118 (3)	−18 (3)
N(1)	349 (4)	350 (5)	269 (4)	−79 (4)	79 (3)	38 (3)
O(2)	366 (4)	350 (4)	352 (4)	−108 (3)	113 (3)	23 (3)
N(3)	298 (4)	325 (5)	292 (4)	−70 (3)	75 (3)	−37 (3)
N(4)	305 (4)	338 (5)	192 (3)	−43 (4)	18 (3)	1 (3)
N(6)	401 (5)	325 (4)	189 (3)	−125 (4)	84 (3)	−25 (3)
C(7)	269 (4)	288 (4)	178 (3)	−55 (3)	57 (3)	−19 (3)
C(8)	245 (4)	252 (4)	203 (3)	−24 (3)	58 (3)	1 (3)
C(9)	217 (3)	247 (4)	216 (4)	−7 (3)	52 (3)	−24 (3)
N(10)	440 (5)	504 (7)	174 (3)	−207 (5)	49 (3)	−21 (4)

Hydrogen atoms

	H(10*a*)	H(10*b*)	H(4)
10^3U	31 (6)	20 (5)	30 (6)

Discussion of the structure

The furazan ring is planar and quasi-coplanar with the thiadiazine ring (Table 3), and it has different values for the two N–O distances (1·408 *versus* 1·366 Å) although both are essentially single bonds. All distances and angles in the ring lie within the limits found by Cameron & Prout (1969) for furazan rings. The thiadiazine ring exhibits an envelope conformation (Table 4) as in the compounds previously reported (Foces-Foces *et al.*, 1975).

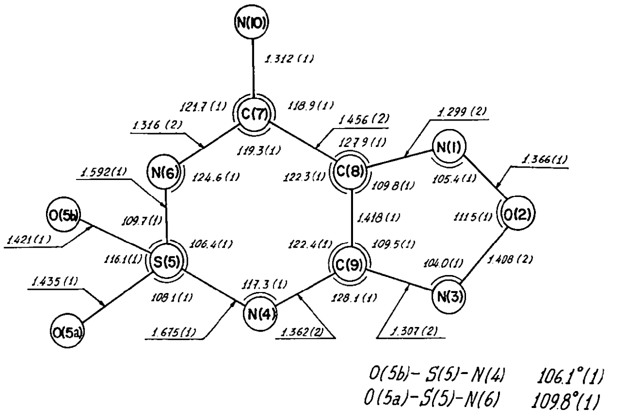

Fig. 1. Bond lengths (Å) and valence angles (°) with their estimated standard deviations referred to the last significant digits.

Table 3. *Deviations* (Å) *of the atoms from some least-squares planes in the molecule, with their dihedral angles*

The equations of the planes are in the form $AX+BY+CZ+D=0$, where X,Y,Z are coordinates referred to the orthogonal axes, with X parallel to **a**, Y perpendicular to **a** in the plane of **a** and **c** and Z perpendicular to the plane of **a** and **c**. (* denotes the atoms used in the plane calculations).

Plane 1		Plane 2	
N(4)	0·025*	N(1)	0·003*
S(5)	−0·416	O(2)	−0·002*
O(5*b*)	0·381	N(3)	0·000*
O(5*a*)	−1·837	C(8)	−0·003*
N(6)	−0·031*	C(9)	0·002*
C(7)	0·036*		
C(8)	−0·009*		
C(9)	−0·022*		
N(10)	0·200		

Plane 1: $0·7540X-0·6398Y-0·1490Z+0·2121=0·0$

Plane 2: $0·7552X-0·6412Y-0·1356Z+0·1718=0·0$

$\angle$(Plane 1) (Plane 2) 0·8°

Table 4. *Torsion angles*

S(5)–N(6)–C(7)–C(8)	11·31°
C(8)–C(9)–N(4)–S(5)	−20·22
N(6)–C(7)–C(8)–C(9)	4·88
C(7)–C(8)–C(9)–N(4)	−0·89
C(9)–N(4)–S(5)–N(6)	30·46
N(4)–S(5)–N(6)–C(7)	−27·10

Irrespective of the method used for the interpretation of distances in terms of bond orders (Pauling 1960; Herbstein & Schmidt, 1955; Donohue, Lavine & Rollett, 1956; Cruickshank, 1961; Sabesan & Venkatesan, 1971) a certain localization of π-bonding was always obtained in an approximate way. Thus, the intermediate character for the bonds in the sulphone group could most probably be due to some degree of polarization, leaving the S atom with a deficiency of electrons. This polar effect ought to be neutralized by the neighbouring nitrogen atoms, especially by the one which is more engaged in the π-bonding, N(6). From this we could establish some canonical forms:

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31058 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

these are illustrated in Fig. 2. In the second canonical form [Fig. 2(*b*)], the electron pair for the aminic nitrogen atom could compensate the electronic deficiency of C(7). Consequently, the hydrogen atoms [H(10*a*) and H(10*b*)] should have some acid character, with a capacity for forming hydrogen bonds [Fig. 2(*c*)].

The charge distribution on the six-membered ring seems to have little influence on the five-membered ring. Here, the π-bonding system is highly localized, in contrast to other structures previously reported (Foces-Foces *et al.*, 1975*a*, *b*) [see the triazolo ring in Fig. 3(*a*)] in which the π-system was much more delocalized. The shortening of the N(4)–C(9) distance could be caused by the electronegative character assigned to the central atom in the pentagonal ring, which in turn would be due to its low charge density due to electron sharing with N(1). This might also explain the shortening of the O(2)–N(1) distance.

For the compounds with the triazolo ring, N(1) could contribute to the neutralization of the low electronic density for the aminic carbon C(7) already mentioned. The electronic deficiency for N(1) would be neutralized by some electron sharing with N(2). The latter would be followed by a delocalization of the π electrons of N(3) giving rise to the canonical forms of Fig. 3. Accordingly, the pentagon would present an electron delocalization, with N(4) contributing to it and the hydrogen attached to N(2) having a proton-donor character.

From the present structure and the two previously reported (Foces-Foces *et al.*, 1975*a*,*b*) we conclude for the six-membered ring that: (*a*) the S–O bonds are partially polarized, (*b*) the double-bond character for S(5)–N(6) is consequently increased, and so is the order for C(7)–N(10) and C(7)–C(8), while that for N(6)–C(7) is lowered, and (*c*) the double-bond character for N(4)–C(9) may depend on the electronegativity of the central atom of the pentagonal moiety.

Packing

The intermolecular packing within the crystal is due to van der Waals forces and weak hydrogen interac-

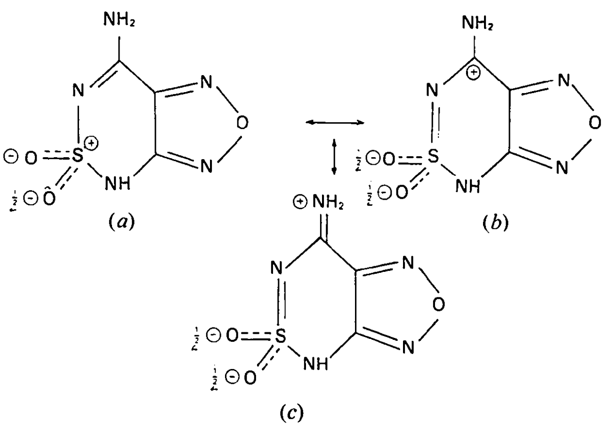

Fig. 2. Some main canonical diagrams for the title compound.

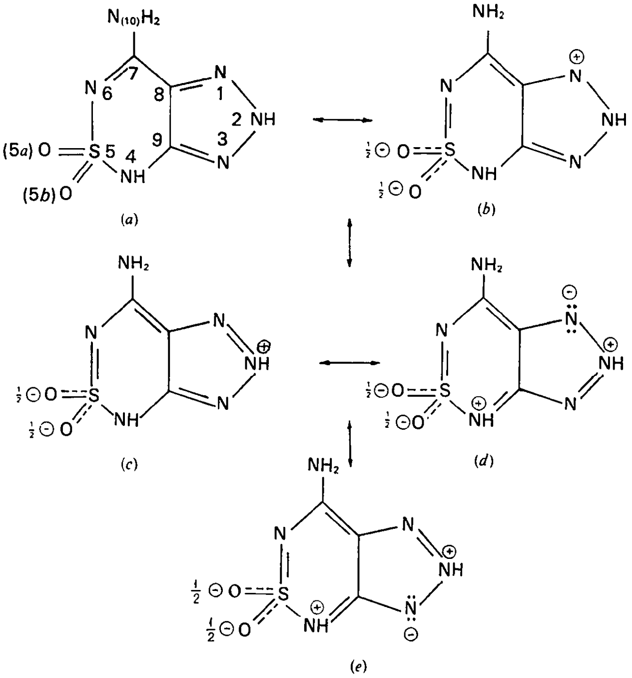

Fig. 3. Some main canonical diagrams for the triazolo moiety.

Table 5. *Hydrogen bonds, short X*–H··· *Y van der Waals contacts and group features* (X_a, X'_a, Y_a, Y'_a *are the bonded atoms to X and Y respectively; distances are in* Å *and angles in degrees with the e.s.d.'s from least squares in parentheses*)

X'_a	X_a	X	H	Y	Y_a	Y'_a
C(9) (*A*)	S(5) (*A*)	N(4) (*A*)	H(4) (*A*)	N(3) (*B*)	O(2) (*B*)	C(9) (*B*)
–	C(7) (*A*)	N(10) (*A*)	H(10*a*) (*A*)	O(5*a*) (*C*)	S(5) (*C*)	–
–	C(7) (*A*)	N(10) (*A*)	H(10*b*) (*A*)	O(5*a*) (*D*)	S(5) (*D*)	–
	Distances			Angles		
$X\cdots Y$	X–H	H$\cdots Y$	X–H$\cdots Y$	H–$X\cdots Y$	H–X–X_a	H–X–X'_a
3·040 (1)	0·85 (3)	2·26 (3)	152 (3)	20 (2)	110 (2)	125 (2)
2·877 (2)	0·90 (3)	2·00 (3)	165 (3)	10 (2)	119 (2)	–
2·971 (2)	0·86 (3)	2·16 (3)	159 (2)	15 (2)	119 (2)	–

Symmetry code

(*A*)	x	y	z	(*C*)	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
(*B*)	$-x$	$-y$	$-z$	(*D*)	x	$\frac{1}{2}-y$	$-\frac{1}{2}+z$

tions. All the intermolecular distances less than 3·3 Å were calculated and some of them were shorter than expected for standard van der Waals values. In fact, the short contacts involving hydrogen atoms are of type N···O and N···N. The two contacts shorter than 3·0 Å are those from N(10) (in molecule *A*) to O(5*a*) (in molecule *C*), and from N(10) (*A*) to O(5*a*) (*D*), and have values of 2·877 and of 2·971 Å respectively. There exists another contact of 3·040 Å between N(4) (*A*) and N(3) (*B*). The symmetry involved and the translational operations are presented in Table 5. There are no large deviations from linearity. One could explain the N(4)···N(3) interaction as being responsible for the longer distance N(3)–O(2) in contrast to the shorter O(2)–N(1) distance. There are also other shorter contacts not involving hydrogen atoms, such as O(5*b*)···N(2) of 3·088 Å, O(5*b*)···C(9) of 3·059 Å, O(2)···N(1) of 3·036 Å and O(2)···O(2) of 3·024 Å. These distances have values very close to the sum of the van der Waals radii.

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Structural Chemistry of the Benzotropone System. II.* The Crystal and Molecular Structure of 4,5-Benzotropone

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Crystals of 4,5-benzotropone, $C_{11}H_8O$, are monoclinic, space group $P2_1/c$, with unit-cell dimensions $a=6·250$ (3), $b=7·757$ (2), $c=17·120$ (6) Å, $\beta=100·65$ (3)°, $Z=4$. Intensities were collected on Weissenberg photographs and by four-circle diffractometry. The photographic data were measured on a densitometer. The structure was solved by the direct method and refined by the full-matrix least-squares method. The final R value was 0·072 for densitometer data and 0·046 for diffractometer data. The molecule is approximately planar. The C=O bond length is 1·235 Å. The aromaticity is related satisfactorily to the bond alternation in the seven-membered ring and C=O bond length. The effects of bond-angle strain on bond lengths are examined.

Introduction

On the basis of the high dipole moment of 4,5-benzotropone (I*a*), 4·70–4·88 D (Gäumann, Schmid & Heilbronner, 1956; Shimozawa, Kumakura, Hoshino & Ebine, 1971), it has been assumed that the ionic form (I*b*) satisfying Hückel's $4n+2$ π rule contributes substantially to the ground-state resonance hybrids. The spectral (Meuche, Strauss & Heilbronner, 1958) and thermochemical (Schmid, Kloster-Jensen, Kováts & Heilbronner, 1956) studies showed the presence of some aromaticity of this compound, although it was

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