3-Hydroxy-4-nitro-6*H*-1,2,6-thiadiazine 1,1-Dioxide

BY C. ESTEBAN-CALDERÓN, M. MARTÍNEZ-RIPOLL AND S. GARCÍA-BLANCO

Departamento de Rayos X, Instituto Rocasolano, Serrano 119, Madrid-6, Spain

Abstract. $C_3H_3N_3O_5S$, $M_r = 193\cdot2$, monoclinic, $P2_1/c$, $a = 12\cdot796$ (1), $b = 5\cdot2427$ (1), $c = 9\cdot7408$ (3) Å, $\beta = 103\cdot272$ (3)°, $V = 636\cdot0$ (1) Å^3, $Z = 4$, $D_c = 2\cdot02$ Mg m^{-3}, μ(Mo $K\alpha$) $= 0\cdot494$ mm^{-1}. The structure has been refined to $R = 0\cdot034$ for 1642 independent reflexions. The thiadiazine ring presents an envelope conformation, the S atom being at the flap. The molecules are held together by hydrogen bonds.

Introduction. A sample of the title compound was supplied by Drs Stud and Goya (Instituto de Química Médica, CSIC, Madrid). Prismatic single crystals of this compound were analysed on a four-circle diffractometer, equipped with graphite-mono-chromated Mo $K\alpha$ radiation ($\lambda = 0\cdot71069$ Å). The lattice constants were obtained after least-squares fit of the 2θ values corresponding to the centre of gravity of 30 reflexions measured for both positive and negative 2θ angles. 1807 unique reflexions were collected up to $\theta = 30°$ with an $\omega/2\theta$ scan. Of these, 1642 were considered as observed with $I > 2\sigma(I)$, and were used in the remaining calculations. No crystal decomposition was detected. Intensity data were corrected for absorption effects with *ORABS* (Schwarzenbach, 1972). Scattering factors for neutral atoms and

anomalous-dispersion corrections for S were taken from *International Tables for X-ray Crystallography* (1974).

The structure was solved by *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). Most of the remaining calculations were performed with the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). All H atoms were located on a difference synthesis calculated for reflexions with $\sin \theta/\lambda < 0\cdot5$ Å^{-1}. Structure refinement was done by full-matrix least-squares methods. The function minimized was $\sum w|\Delta F|^2$ with $w = 1$ until convergence was achieved. In further steps of refinement a weighting scheme of the type $w = w_1 w_2$, with $w_1 = K/(a + b|F_o|)^2$ and $w_2 = 1/(c + d \sin \theta/\lambda)$ (Martínez-Ripoll & Cano, 1975), was chosen to prevent bias on $\langle w|\Delta F|^2 \rangle$ *vs* $\langle F_o \rangle$ and *vs* $\langle \sin \theta/\lambda \rangle$.* Final refinement, with variable isotropic temperature factors for H atoms, converged to $R = 0\cdot034$ and $R_w = 0\cdot034$. Table 1 shows the final atomic parameters.*

Discussion. The present study originated from a previous work by Goya & Stud (1978). It has been carried out to clarify the tautomeric form of this compound as present in the solid state and in order to compare its molecular geometry with the one present in the anionic form in both sodium and potassium salts (Esteban-Calderón, Martínez-Ripoll & García-Blanco, 1982*a,b*).

Fig. 1 shows a perspective drawing of the molecule, where some symmetrically related atoms are also shown for clarity. Interatomic contacts are represented by dashed lines. The bond distances and angles (Table 2) could indicate electron delocalization within the thiadiazine ring, implying variable bond orders. The length S–N(1), 1·674 Å, is close to the value for an S–N single bond (Gillespie, Ireland & Vekris, 1975), while the distance S–N(2), 1·574 Å, implies a bond

Table 1. *Atomic coordinates and isotropic temperature factors* (Å$^2 \times 10^3$)

$$U_{eq} = \tfrac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

	x	y	z	U_{eq}
S	0·12600 (2)	0·80074 (5)	0·96395 (3)	19
C(1)	0·19050 (9)	1·15234 (21)	0·80834 (12)	22
C(2)	0·28482 (8)	1·02349 (21)	0·81613 (11)	21
C(3)	0·31091 (9)	0·80094 (21)	0·90427 (12)	23
N(1)	0·11766 (8)	1·07845 (19)	0·87733 (11)	25
N(2)	0·24467 (8)	0·70747 (20)	0·97576 (12)	27
N(3)	0·35636 (9)	1·12473 (22)	0·73570 (11)	27
O(1)	0·10817 (7)	0·85692 (19)	1·10096 (9)	27
O(2)	0·05076 (8)	0·62952 (19)	0·87966 (10)	30
O(3)	0·40184 (9)	0·67797 (25)	0·91981 (14)	40
O(4)	0·32793 (10)	1·30638 (23)	0·65817 (13)	39
O(5)	0·44476 (9)	1·02135 (26)	0·74758 (15)	42
				U
H(O3)	0·434 (3)	0·743 (7)	0·869 (4)	28 (6)
H(N1)	0·062 (3)	1·162 (6)	0·868 (3)	23 (6)
H(C1)	0·175 (2)	1·304 (5)	0·755 (3)	13 (5)

order of ~1·5. The S—O lengths are typical for most thiadiazine compounds (Cabezuelo, Cano, Foces-Foces & García-Blanco, 1977; Esteban-Calderón, Martínez-Ripoll & García-Blanco, 1979).

Table 3 shows some torsion angles, and Table 4 contains the atomic deviations from several molecular planes. The thiadiazine ring can be described as envelope 2,3-diplanar according to the six-ring conformational model (Cano, Foces-Foces & García-Blanco, 1977).
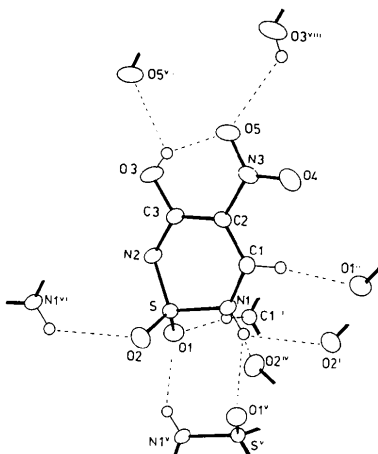

Fig. 1. Perspective drawing (Johnson, 1965) of the molecule. Some symmetrically related atoms are also shown. For symmetry operations, see Table 5. Thermal ellipsoids are scaled to 50% probability.

Table 3. *Torsion angles* (°) *with e.s.d.'s in parentheses*

N(2)–S–N(1)–C(1)	14·5 (1)	C(1)–C(2)–N(3)–O(5)	175·7 (1)
S–N(1)–C(1)–C(2)	−8·1 (1)	C(1)–C(2)–N(3)–O(4)	−4·9 (1)
N(1)–C(1)–C(2)–C(3)	−1·6 (1)	O(3)–C(3)–C(2)–N(3)	1·4 (1)
C(1)–C(2)–C(3)–N(2)	2·6 (1)	C(3)–C(2)–N(3)–O(5)	−2·8 (1)
C(2)–C(3)–N(2)–S	7·0 (1)	C(1)–N(1)–S–O(1)	131·8 (1)
C(3)–N(2)–S–N(1)	−13·9 (1)	C(1)–N(1)–S–O(2)	−103·7 (1)

Table 4. *Atomic deviations* (Å) *from least-squares planes* (*Nardelli, Musatti, Domiano & Andreetti*, 1965) *with e.s.d.'s in parentheses*

Atoms marked with asterisks are not included in the calculation.

Plane 1		Plane 2	
C(1)	0·002 (1)	O(3)	−0·004 (1)
C(2)	−0·009 (1)	C(3)	−0·001 (1)
C(3)	0·012 (1)	C(2)	0·009 (1)
N(1)	0·002 (1)	N(3)	−0·014 (1)
N(2)	−0·007 (1)	O(5)	0·010 (1)
*S	−0·212 (1)	*O(4)	−0·066 (1)
*O(1)	0·824 (1)	*HO(3)	−0·06 (3)
*O(2)	−1·551 (1)		
*O(3)	0·059 (1)		
*N(3)	−0·010 (1)		
*O(4)	−0·089 (1)		
*O(5)	0·062 (1)		

Angle between planes 1/2 = 2·2 (2)°.

The molecules are linked through hydrogen bonds (Fig. 1 and Table 5). The hydroxyl group takes part in an asymmetrically bifurcated hydrogen bond (inter- and intramolecular). N(1)—H also forms an asymmetric hydrogen bond, bifurcated or possibly trifurcated (Schuster, Zundel & Sandorfy, 1976). A short inter-

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

S–O(1)	1·435 (1)	C(2)–C(3)	1·442 (2)
S–O(2)	1·430 (1)	C(2)–N(3)	1·436 (2)
S–N(1)	1·674 (1)	C(3)–N(2)	1·309 (2)
S–N(2)	1·574 (1)	C(3)–O(3)	1·308 (2)
N(1)–C(1)	1·326 (2)	N(3)–O(4)	1·218 (2)
N(1)–H	0·83 (3)	N(3)–O(5)	1·236 (2)
C(1)–C(2)	1·370 (2)	O(3)–H	0·79 (4)
C(1)–H	0·95 (2)		
O(1)–S–O(2)	115·7 (1)	N(1)–C(1)–C(2)	122·7 (1)
O(1)–S–N(1)	106·6 (1)	N(1)–C(1)–H	116 (2)
O(1)–S–N(2)	110·6 (1)	C(2)–C(1)–H	121 (2)
O(2)–S–N(1)	107·5 (1)	C(1)–C(2)–C(3)	120·8 (1)
O(2)–S–N(2)	111·0 (1)	N(3)–C(2)–C(1)	116·8 (1)
N(1)–S–N(2)	104·8 (1)	N(3)–C(2)–C(3)	122·3 (1)
S–N(1)–C(1)	122·6 (1)	N(2)–C(3)–O(3)	114·9 (1)
S–N(1)–H	118 (2)	C(2)–C(3)–N(2)	122·0 (1)
C(1)–N(1)–H	119 (2)	C(2)–C(3)–O(3)	123·1 (1)
S–N(2)–C(3)	125·2 (1)	C(3)–O(3)–H	107 (2)
C(2)–N(3)–O(4)	119·4 (1)		
C(2)–N(3)–O(5)	118·1 (1)		
O(4)–N(3)–O(5)	122·5 (1)		

Table 5. *Intermolecular contacts*

X–H···Y	X···Y	X–H	H···Y	X–H···Y
Hydrogen bonds				
Intramolecular				
*O(3)–H···O(5)	2·604 (2) Å	0·79 (4) Å	1·90 (4) Å	148 (4)°
Intermolecular				
†N(1)–H···O(2ⁱᵛ)	2·916 (1)	0·83 (3)	2·52 (3)	111 (2)
†N(1)–H···O(1ᵛ)	2·965 (1)	0·83 (3)	2·27 (3)	143 (3)
†N(1)–H···O(2ⁱ)	3·015 (1)	0·83 (3)	2·46 (3)	126 (3)
*O(3)–H···O(5ᵛⁱⁱ)	2·942 (2)	0·79 (4)	2·42 (4)	125 (3)
Other contacts				
C(1)–H···O(1ⁱⁱ)	3·291 (1)	0·95 (2)	2·35 (2)	170 (2)
O(1)···O(2ⁱˣ)	2·972 (1)			
O(5)···O(2ᵛⁱⁱ)	2·973 (2)			
O(5)···O(4ᵛⁱⁱ)	3·057 (2)			

Symmetry operations: (i) x, $1 + y$, z; (ii) $x, \frac{3}{2} - y, -\frac{1}{2} + z$; (iii) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (iv) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (v) $-x$, $2 - y$, $2 - z$; (vi) x, $-1 + y$, z; (vii) $1 - x$, $-\frac{1}{2} + y, \frac{3}{2} - z$; (viii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ix) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

* Bifurcated hydrogen bond.
† Doubtful trifurcated hydrogen bond.

molecular contact of type C(1)—H···O(1) occurs in this compound with an H···O(1) distance of 2·35 Å (the sum of the van der Waals radii being 2·5 Å) and an angle C(1)—H···O(1) of 170°. Several examples of short C···O distances have been summarized by Sutor (1963) and later discussed by Rich & Davidson (1968) with a view to rejecting them as true hydrogen bonds. However, according to severe geometrical considerations (Table 5) and regarding some recent examples (Martínez-Ripoll & Lorenz, 1974, 1976), this C—H···O contact could be accepted as a hydrogen bond.

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Structure of Octafluoro-4,4'-bis(phenylethynyl)biphenyl*

By NEIL GOODHAND AND THOMAS A. HAMOR

Department of Chemistry, University of Birmingham, Birmingham B15 2TT, England

Abstract. $C_{28}H_{10}F_8$, $M_r = 498·4$, monoclinic, $C2/c$, $a = 23·86$ (2), $b = 6·22$ (1), $c = 14·98$ (1) Å, $\beta = 100·01$ (5)°, $U = 2189$ Å^3, $Z = 4$, $D_c = 1·51$ Mg m^{-3}; molecular symmetry C_2. The structure was refined to $R = 0·042$ for 1387 observed counter amplitudes. The acetylenic triple-bond length is 1·187 (3) Å. The inter-ring bond of the octafluorobiphenyl system is 1·477 (4) Å and the inter-ring dihedral angle 56·7 (3)°.

Introduction. In earlier papers of this series, the structures of a number of fluorinated biphenyls (Hamor & Hamor, 1978; Goodhand & Hamor, 1978; Brock, Naae, Goodhand & Hamor, 1978) and of perfluorodiphenylethyne (Goodhand & Hamor, 1979) have been described and compared with hydrocarbon analogues. Of particular interest in the biphenyls has been the absence of any relationship between dihedral angle and the length of the inter-ring bond (Goodhand, Hamor & Hamor, 1978). We now report the crystal structure of octafluoro-4,4'-bis(phenylethynyl)biphenyl (Coe, Tatlow & Terrell, 1967) as part of a continuing study of fluorinated biphenyls and of the effect of fluorinated phenyl groups on an adjacent acetylenic triple bond.