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## The Crystal and Molecular Structure of an Analogue of Purine: 4-Amino-*N*<sup>1</sup>,*N*<sup>7</sup>-dimethylimidazo[4,5-*c*]-1,2,6-thiadiazine 1,1-Dioxide (C<sub>6</sub>H<sub>9</sub>N<sub>5</sub>O<sub>2</sub>S)

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The crystals are monoclinic, space group  $P2_1/c$ , cell dimensions:  $a = 7.726$  (1),  $b = 8.657$  (1),  $c = 14.002$  (2) Å,  $\beta = 97.94$  (1)°. 2682 independent reflexions were measured on an automatic diffractometer. The crystal structure was solved by the heavy-atom technique and refined by least-squares methods to  $R = 0.063$ . The sulphone group has a distorted tetrahedral conformation. The sulphur atom deviates from the plane through the other five atoms of the ring by 0.66 Å. This plane is coplanar with that through the imidazole ring and this ring is also planar. The methyl group attached to the imidazole ring is coplanar with it but the methyl group substituted on the thiadiazine ring is not in the plane of this last ring.

### Introduction

The chemical study of 4-amino-*N*<sup>1</sup>,*N*<sup>7</sup>-dimethylimidazo[4,5-*c*]-1,2,6-thiadiazine 1,1-dioxide has been carried out by G. Muñoz and M. Stud (Instituto de Química Médica, CSIC, Madrid) as part of a research project on new heterocyclic compounds containing the thiadiazine group aimed at obtaining substances with biological activity. A crystallographic study of the title compound is especially interesting with regard to conformation of the N-SO<sub>2</sub>-N group, positions of the substituent groups and subsequent comparison with the structures of similar compounds.

### Experimental

A single crystal of dimensions 0.2 × 0.2 × 0.3 mm was selected for X-ray investigations. The density was determined in a mixture of benzene and methylene iodide. The lattice constants were obtained from a least-squares analysis of 34 reflexions measured on a four-circle diffractometer with Mo *K* $\alpha$  radiation. The unit-cell dimensions and other pertinent crystal data are included in Table 1.

The intensity data were collected on a Philips PW 1100 four-circle diffractometer. Intensities were recorded in the  $\omega/2\theta$  scan mode with  $\theta$  between 2 and

Table 1. *Crystal data*

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

Molecular formula	C <sub>6</sub> H <sub>9</sub> N <sub>5</sub> O <sub>2</sub> S
Molecular weight	215.241
System	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i>	7.726 (1) Å
<i>b</i>	8.657 (1)
<i>c</i>	14.002 (2)
$\beta$	97.94 (1)°
<i>Z</i>	4
<i>V</i>	934.6 Å <sup>3</sup>
<i>D</i> <sub>m</sub>	1.50 g cm <sup>-3</sup>
<i>D</i> <sub>c</sub>	1.52
<i>F</i> (000)	448
$\lambda$ (Mo <i>K</i> $\alpha$ )	0.7107 Å

30°; graphite-monochromated Mo *K* $\alpha$  radiation was used. 2682 reflexions were measured of which 2184 had intensities greater than 2 $\sigma$ ,  $\sigma$  being the standard deviation calculated from the counting statistics of the measurements. The intensity data were corrected for Lorentz-polarization and dispersion effects. No absorption correction was applied.

### Solution and refinement of the structure

The S position was deduced from a sharpened Patterson map with Harker peaks. An electron density map phased with the S atom revealed a chemically reasonable fragment of ten new atoms. The remainder of the structure was found in a subsequent map, phased with these 11 atoms. Full-matrix least-squares refinements with unit weights gave an *R* value of 0.09.

The H atoms were located in a difference synthesis and refined isotropically. The data were refined to a stage at which no parameter shift was significant.

An examination of the  $\langle w\Delta^2 \rangle$  ( $\Delta = F_o - F_c$ ) values as a function of  $|F_o|$  and  $\sin \theta$  suggested that the best

Table 2. *Positional parameters of the heavy atoms* ( $\times 10^5$ )

	<i>x</i>	<i>y</i>	<i>z</i>
S(1)	80806 (7)	89787 (6)	40190 (4)
N(2)	63352 (28)	85531 (23)	33045 (15)
C(3)	58598 (28)	70803 (25)	32186 (15)
N(4)	63593 (29)	43905 (23)	39493 (15)
C(5)	71498 (35)	39774 (28)	47990 (18)
N(6)	78805 (27)	51881 (23)	53344 (14)
N(7)	80306 (26)	79589 (23)	50276 (14)
C(8)	75045 (28)	64622 (24)	47837 (15)
C(9)	65791 (28)	59795 (25)	39352 (15)
O(10)	95921 (26)	84698 (24)	36273 (15)
O(11)	79823 (31)	105664 (22)	42647 (17)
N(12)	46521 (28)	66750 (28)	25038 (16)
C(13)	88644 (41)	51079 (38)	62991 (19)
C(14)	73480 (57)	87113 (41)	58360 (27)

Table 3. *Atomic parameters of the hydrogen atoms*

Listed thermal parameters have been multiplied by 10<sup>5</sup>, positional parameters by 10<sup>3</sup>.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(51)	732 (4)	293 (4)	507 (2)	21 (7)
H(121)	443 (5)	581 (5)	243 (2)	22 (8)
H(122)	427 (4)	746 (4)	209 (2)	16 (7)
H(131)	918 (7)	403 (7)	645 (4)	54 (13)
H(132)	818 (6)	545 (5)	674 (3)	39 (10)
H(133)	988 (7)	583 (6)	636 (4)	52 (13)
H(141)	786 (6)	969 (6)	595 (3)	41 (11)
H(142)	595 (8)	884 (6)	571 (4)	58 (14)
H(143)	726 (12)	809 (12)	631 (7)	108 (29)

weighting scheme was  $w = w_1 w_2$  where  $w_1 = 1/\sigma_1^2$  and  $w_2 = 1/\sigma_2^2$ , with  $\sigma_1 = 0.48 + 0.10|F_o|$  when  $|F_o| < 10.02$  and  $\sigma_1 = -0.04 + 0.03|F_o|$  when  $|F_o| > 10.02$  and  $\sigma_2^2 = 2.71 + 2.10|\sin \theta/\lambda|$ . The final unweighted and weighted agreement indices for the observed reflexions were  $R = 0.063$  and  $R_w = 0.070$  respectively, where  $R_w = (\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$ .

The positional coordinates, together with their standard deviations, for the heavy atoms are listed in Table 2; parameters of the H atoms are in Table 3.\* Atomic scattering and dispersion factors were taken from *International Tables for X-ray Crystallography* (1974).

### Discussion

A schematic drawing of the structure with the labelling of the atoms, bond distances and bond angles is given in Fig. 1.

Least-squares planes were calculated through the imidazole ring and through the N(2), C(3), N(7), C(8) and C(9) atoms of the thiadiazine ring, and the results are summarized in Table 4.

The imidazole ring is planar and quasi-coplanar with the thiadiazine ring, excluding the S atom. The deviation of this atom from the plane through the other five atoms is 0.66 Å; this value is larger than the corresponding distances in compounds previously reported (Foces-Foces, Cano & García-Blanco, 1975*a,b*; Foces-Foces, Cano, García-Blanco & Rodríguez, 1975).

The coordination polyhedron of the S atom is a distorted tetrahedron with an O-S-O angle of 117.8°, greater than the tetrahedral value; the remaining angles around the S atom have values close to this value. The non-bonded distances in the tetrahedron are:

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32579 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

O(10)⋯O(11) = 2.444, O(10)⋯N(2) = 2.496, O(10)⋯N(7) = 2.487, O(11)⋯N(2) = 2.455, O(11)⋯N(7) = 2.504 and N(2)⋯N(7) = 2.641 Å. The S(1)—O(10) and S(1)—O(11) bond lengths (1.428 and 1.426 Å respectively) are in good agreement with the values found in other sulphone groups (Prelesnik & Nowacki, 1975).

The present compound shows an arrangement of the bond lengths and angles that enables one to discuss a possible electronic distribution in the molecule.

The intermediate character for the bonds in the sulphone group (Fig. 2) could be due to some degree of polarization, leaving the S(1) atom with a deficiency of electrons (Fig. 2a). This polar effect ought to be neutralized by the delocalization of the π-electron pair of the N(2)—C(3) double bond leaving the C(3) atom with a deficiency of charge (Fig. 2b). This electronic deficiency could be delocalized in two different ways (Fig. 2c and d). The (c) canonical form would justify

the shortening of the C(3)—N(12) bond, with the localization of a positive charge on the N(12) atom, in agreement with the planarity of the NH<sub>2</sub> group and the acid character of the H atoms of the group. The canonical form of Fig. 2 (d) would locate a positive charge on the C(8) atom and would justify the double-bond character of N(7)—C(8). Moreover, the weak double-bond character of C(3)—C(9) and the deviation of the S(1) atom from the plane through the hexagonal ring would indicate a minor contribution of the Fig. 2(d) canonical form, which would require the planarity of the ring. Consequently, the canonical forms Fig. 2(b) and (c) are in better agreement with the results obtained in the resolution of the structure.

Table 4. Deviations (Å) of the atoms from two least-squares planes in the molecule

Atoms included in plane calculations are denoted by an asterisk.

	Plane 1 <i>d</i> (Å)	Plane 2 <i>d</i> (Å)
S(1)	-0.687	-0.658
N(2)	-0.009	-0.033*
C(3)	0.111	0.054*
N(4)	-0.002*	-0.072
C(5)	0.003*	-0.034
N(6)	-0.004*	0.007
N(7)	-0.038	0.010*
C(8)	0.002*	0.010*
C(9)	-0.001*	-0.042*
O(10)	-2.089	-2.064
O(11)	-0.276	-0.211
N(12)	0.412	0.308
C(13)	-0.018	0.038
C(14)	1.101	1.183

Plane 1:  $-0.8996X + 0.1402Y + 0.4135Z + 0.8484 = 0.0$

Plane 2:  $-0.9148X + 0.1208Y + 0.3855Z + 1.2101 = 0.0$

Angle (plane 1)/(plane 2) = 177.86°

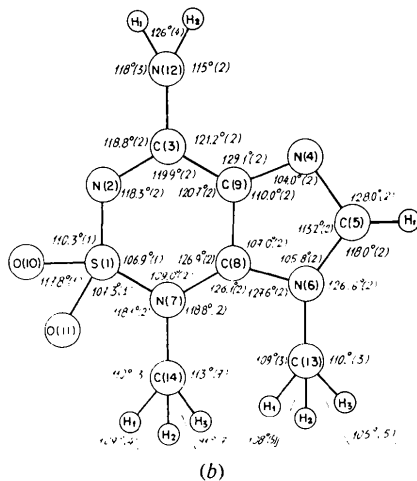
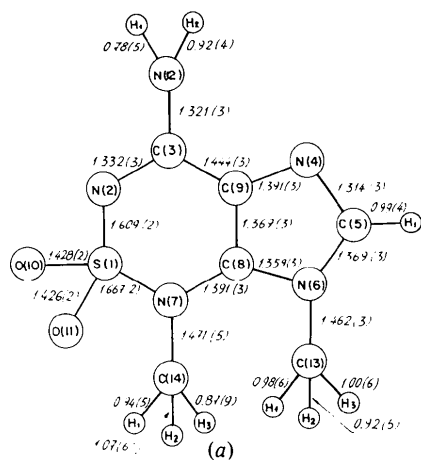


Fig. 1. (a) Bond lengths (Å) and (b) bond angles (°) with their estimated standard deviations in parentheses.

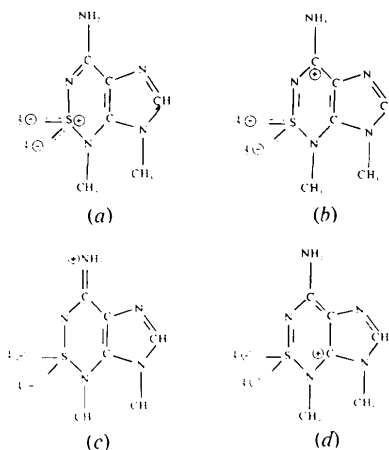


Fig. 2. Some main canonical diagrams for the thiaziazine ring.

Table 5. *Some short intermolecular contacts*

Distances are in Å and angles in degrees, with the e.s.d.'s from least squares in parentheses.

C(3 <sup>i</sup> )...N(12 <sup>i</sup> )...N(2 <sup>ii</sup> )	130.2 (2)	N(12 <sup>i</sup> )...N(2 <sup>ii</sup> )	2.998 (3)
N(12 <sup>i</sup> )...H(121 <sup>i</sup> )...N(2 <sup>ii</sup> )	166 (2)	N(12 <sup>i</sup> )...N(4 <sup>iii</sup> )	3.148 (3)
H(121 <sup>i</sup> )...N(12 <sup>i</sup> )...N(2 <sup>ii</sup> )	15 (3)	C(5 <sup>i</sup> )...O(11 <sup>iv</sup> )	3.145 (3)
C(3 <sup>i</sup> )...N(12 <sup>i</sup> )...N(4 <sup>iii</sup> )	112.3 (2)	O(11 <sup>iv</sup> )...N(12 <sup>iii</sup> )	3.139 (3)
C(3 <sup>i</sup> )...H(122 <sup>i</sup> )...N(4 <sup>iii</sup> )	174 (3)	O(10 <sup>v</sup> )...C(13 <sup>v</sup> )	3.325 (4)
H(122 <sup>i</sup> )...N(12 <sup>i</sup> )...N(4 <sup>iii</sup> )	4 (2)	O(10 <sup>v</sup> )...C(14 <sup>vi</sup> )	3.415 (4)
N(4 <sup>i</sup> )...C(5 <sup>i</sup> )...O(11 <sup>iv</sup> )	97.2 (2)	H(121 <sup>i</sup> )...N(2 <sup>ii</sup> )	2.26 (5)
C(5 <sup>i</sup> )...H(51 <sup>i</sup> )...O(11 <sup>iv</sup> )	129 (3)	H(122 <sup>i</sup> )...N(4 <sup>iii</sup> )	2.23 (4)
H(51 <sup>i</sup> )...C(5 <sup>i</sup> )...O(11 <sup>iv</sup> )	37 (2)	H(51 <sup>i</sup> )...O(11 <sup>iv</sup> )	2.43 (4)
C(3 <sup>i</sup> )...N(12 <sup>i</sup> )...O(11 <sup>iv</sup> )	175 (2)		
S(1 <sup>i</sup> )...N(2 <sup>i</sup> )...N(12 <sup>iii</sup> )	100.2 (1)		
C(5 <sup>i</sup> )...N(4 <sup>i</sup> )...N(12 <sup>iii</sup> )	115.3 (2)		
S(1 <sup>i</sup> )...O(11 <sup>iv</sup> )...C(5 <sup>iii</sup> )	171.2 (2)		
S(1 <sup>i</sup> )...O(11 <sup>iv</sup> )...N(12 <sup>iii</sup> )	98.9 (1)		

## Symmetry code

(i)	$x, y, z;$
(ii)	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z;$
(iii)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z;$
(iv)	$x, -1+y, z;$

(v)	$2-x, 1-y, 1-z$
(vi)	$2-x, 2-y, 1-z$
(vii)	$x, 1+y, z$

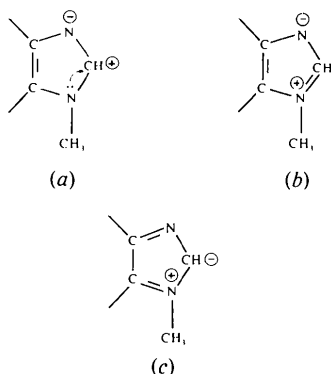


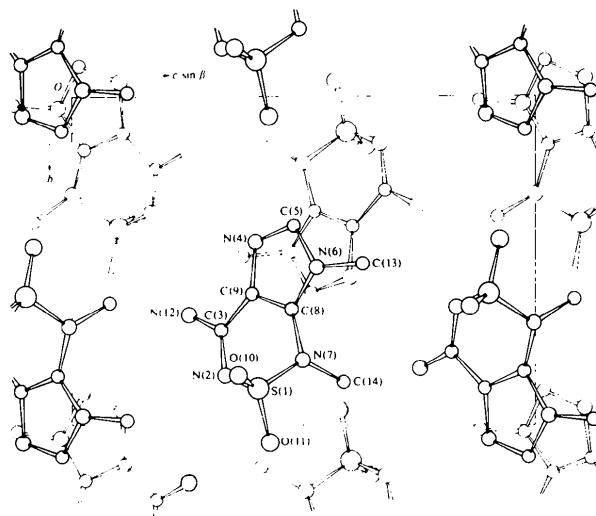
Fig. 3. Some main canonical diagrams for the imidazole ring.

The pentagonal ring shows an aromatic character. Bond distances and angles are in agreement with the results found by Martínez-Carrera (1966) in imidazole and by other authors in compounds in which the imidazole ring is included (Ducruix & Pascard-Billy, 1975; Form, Raper & Downie, 1976; Shieh & Voet, 1975). The charge distribution on the six-membered ring seems to have no influence on the five-membered ring. Moreover, the aromatic character of the pentagonal ring could be considered as an effect of localization of the  $\pi$  electrons of the N(4)–C(5) bond on the N(4) atom, and the delocalization of the positive charge on the C(5) atom would give as a result the canonical forms of Fig. 3(a), (b), (c). The two last forms localize the positive charge on N(6) because of the electron-donating character of the CH<sub>3</sub> group. Moreover, the last form, Fig. 3(c), seems to be of little importance. All polarization effects affect the molecular packing. A view of the structure along *a* illustrating the arrangement is shown in Fig. 4; Table 5 lists the

distances less than 3.5 Å. The contacts N(12)⋯N(2), N(12)⋯N(4) and C(5)⋯O(11) involving H atoms could be considered as weak hydrogen bonds. There are also some other short contacts: N(12)⋯O(11), O(10)⋯C(13) and O(10)⋯C(14).

The existence of these short contacts in addition to the possible hydrogen bonds could indicate a complete set of weak electrostatic interactions that would bind the molecules together. All such interactions could be explained by consideration of the electrostatic arrangement in the molecule.

In the remainder of the structure there are no inter-

Fig. 4. Projection of the structure along *a*.

molecular separations significantly less than the sum of the respective van der Waals radii.

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## The Crystal Structure of 2-Diphenylmethyl-4,4-diphenyl-6-methyl-4*H*-3,1-benzothiazine

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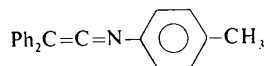
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C<sub>34</sub>H<sub>27</sub>NS, triclinic, *P*1̄ (No. 2), *a* = 9.963 (3), *b* = 14.937 (4), *c* = 9.356 (4) Å, *α* = 90.50 (4), *β* = 105.44 (4), *γ* = 111.02 (4)°, *Z* = 2, *D*<sub>c</sub> = 1.29 g cm<sup>-3</sup>, *μ*(Cu *K*α) = 13.0 cm<sup>-1</sup>. The crystal structure determination has proved that thiobenzophenone (I) and diphenyl-*N-p*-tolylketenimine (II) react to give a substituted 4*H*-3,1-benzothiazine.



(I)



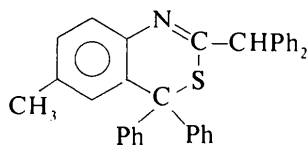
(II)

#### Introduction

The reaction between *N*-arylketenimines and thio-benzophenones leads to 1:1 adducts which appear from spectroscopic data (IR, NMR and MS) to have the structure of 4*H*-3,1-benzothiazine derivatives. While the most common reactivity mode of ketenimine cycloaddition is that occurring on the cumulative C=C or C=N double bond (Krow, 1971), the formation of

the 3,1-benzothiazine must involve the cumulene system *and* the C=C bond of the *N*-aryl ring. In order to provide an unequivocal structure assignment of the observed products, we have carried out the crystal structure determination of the title compound (III) derived from the reaction of thiobenzophenone (I) and diphenyl-*N-p*-tolylketenimine (II). In addition it may be stressed that this is the first structure determination of a 4*H*-3,1-benzothiazine system.

Intensities were collected on an automated Philips PW 1100 diffractometer with monochromated Cu *K*α radiation and the *ω*/2*θ* scan technique. Of the 2012 reflexions collected (*θ* ≤ 45°), 178 having *I*<sub>o</sub> ≤ 2*σ*(*I*<sub>o</sub>) were considered unobserved. Intensities were not corrected for absorption [*μ*(Cu *K*α) = 13.0 cm<sup>-1</sup>; crystal dimensions 0.11 × 0.19 × 0.30 mm]. Lorentz and polarization corrections were applied as usual. Scattering factors for S, C and N atoms were taken



(III)