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The Crystal and Molecular Structure of Sulphur-Containing Heterocyclic Ring Compounds. I. 2-Amino-4-thiazolidinone-5-acetic Acid

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2-Amino-4-thiazolidinone-5-acetic acid, $C_5H_6N_2O_3S$, is monoclinic, space group $P2_1/c$, $Z=4$. The structure was solved by Patterson and minimum methods with 957 visually estimated X-ray reflexions, and refined to an R of 0·11. The 5-membered heterocyclic ring is partially conjugated, and the compound is more in the 2-amino than in the 2-imino form.

Introduction

2-Amino-4-thiazolidinone-5-acetic acid is one of a series of sulphur-containing heterocycles synthesized in the Bio-organic Division of this Research Centre as potential radioprotective agents (Choughuley & Chadha, 1963). The present study was undertaken to determine the conjugation of the 5-membered ring and the nature of the side chain at the 2-position, *i.e.* whether it is 2-amino or 2-imino, and also to deduce the nature of any S···O interaction.

Experimental

The compound crystallizes from aqueous solution as colourless, monoclinic needles. The unit-cell parameters determined from Weissenberg photographs taken with Cu Kα radiation ($\lambda=1{\cdot}542$ Å) are $a=10{\cdot}30$ (2), $b=7{\cdot}32$ (1), $c=12{\cdot}64$ (2) Å, $\beta=128$ (1)°, $Z=4$, $d_o=1{\cdot}50$ g.cm^{-3}, $d_c=1{\cdot}48$ g.cm^{-3}. The systematic absences $h0l$ for l odd and $0k0$ for k odd characterize the space group uniquely as $P2_1/c$ (Amirthalingam & Muralidharan, 1967). Intensities were collected with Cu $K\alpha$ radiation by the equi-inclination Weissenberg method. The reflexions hnl ($n=0$ to 5) and $hk0$ were recorded and a total of 957 unique intensities measured visually. The data were corrected for Lorentz and polarization effects and for spot size, but not for absorption. Initially the scale factors were found from a Wilson plot, as well as by cross-checking with common reflexions.

Structure determination

The structure was solved by a combination of Patterson and minimum methods and refined by the full-matrix least-squares method with anisotropic thermal factors for the sulphur atom only. Cruickshank's weighting scheme $\sigma=A+F_o+CF_o^2$ with $A=5{\cdot}0$ and $C=0{\cdot}03$ was used. The form factors were taken from *International Tables for X-ray Crystallography* (1962). Hydrogen atoms were ignored. The final R for all observed reflexions was 0·11.

A composite view of the structure as obtained from the final Fourier synthesis is shown in Fig. 1. The structure projected down **b** is shown in Fig. 2. The final parameters are given in Table 1 and the structure factors in Table 2. The bond lengths and angles are shown in Fig. 3.

Table 1. *Final coordinates and temperature factors with e.s.d.'s in parentheses*

	x	y	z	B
S	0·1441 (2)	0·2271 (3)	0·3537 (2)	–
O(1)	−0·2145 (7)	0·2246 (9)	0·1195 (6)	3·1 (1)
O(2)	−0·3150 (7)	0·3382 (9)	−0·0895 (6)	2·8 (1)
O(3)	0·2627 (7)	0·0863 (9)	0·1263 (6)	3·0 (1)
N(1)	0·3933 (7)	0·1852 (9)	0·3498 (6)	2·4 (1)
N(2)	0·4661 (9)	0·2931 (9)	0·5599 (6)	2·9 (1)
C(1)	−0·1954 (9)	0·2717 (9)	0·0345 (8)	2·5 (1)
C(2)	−0·0312 (9)	0·2693 (9)	0·0658 (7)	2·4 (1)
C(3)	0·0924 (9)	0·1451 (9)	0·1919 (7)	2·3 (1)
C(4)	0·2565 (9)	0·1338 (9)	0·2170 (7)	2·3 (1)
C(5)	0·3531 (9)	0·2369 (9)	0·4297 (6)	2·3 (1)

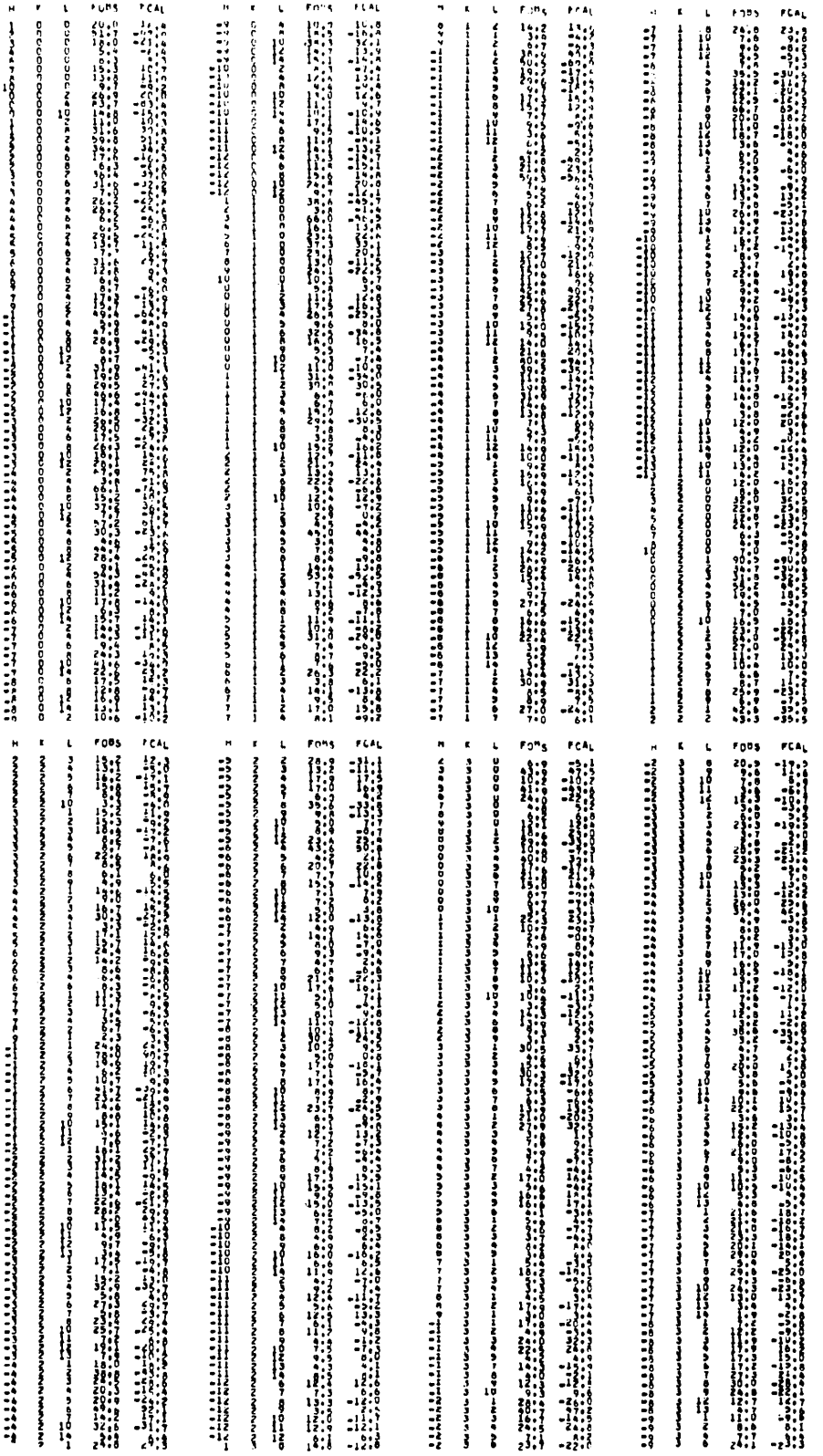
Anisotropic temperature factor for sulphur of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{23}kl+2\beta_{13}hl)]$.

β_{11}	β_{22}	β_{33}	β_{12}
0·0079 (3)	0·0098 (7)	0·0068 (2)	0·0016 (5)
	β_{13}	β_{23}	
	0·0102 (4)	0·0010 (5)	

Description of the structure

The 5-membered ring, the oxygen atom at the 4-position, and the nitrogen atom at the 2-position are coplanar. The equation of the least squares plane is $0{\cdot}0998x+0{\cdot}9471y-0{\cdot}3048z=0{\cdot}3745$. The deviations of the atoms are C(3), 0·004; C(4), 0·007; C(5), 0·007; N(1), 0·014; N(2), 0·007; and O(3), 0·004 Å. The carboxyl group is planar. The equation of the least-squares plane is $0{\cdot}0485x-0{\cdot}9315y-0{\cdot}3604z+2{\cdot}103=0$. Deviations are O(1), 0·009; O(2), 0·007; C(1), 0·020;

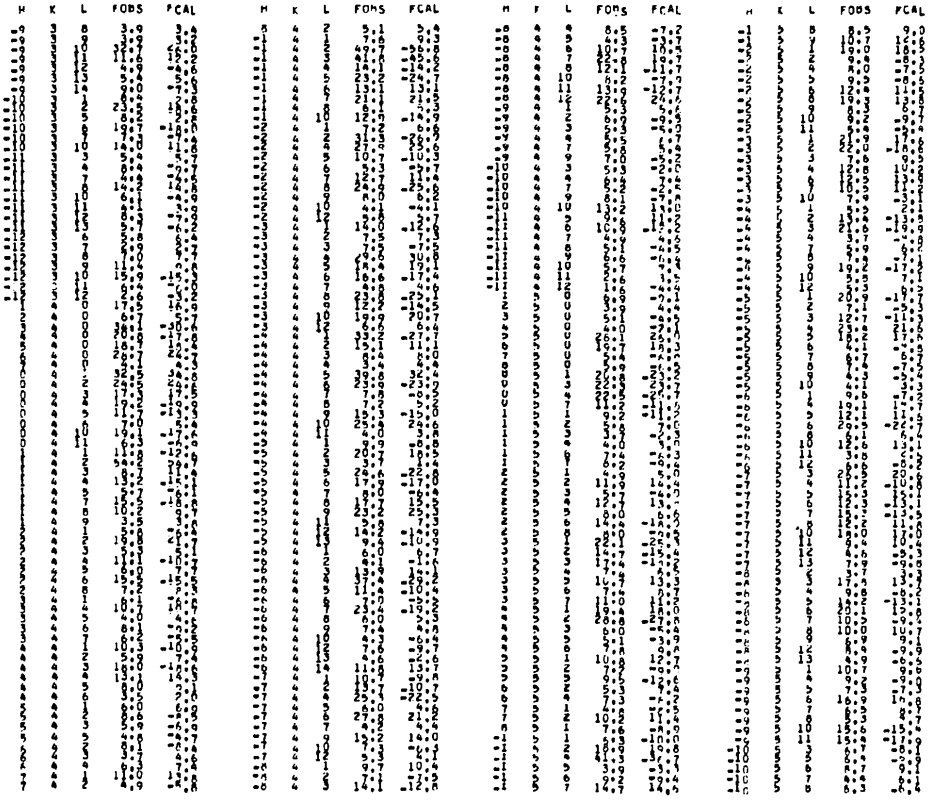
Table 2. *Observed and calculated structure factors*



C(2), 0·007 Å. The angle between these two planes is 143°.

An examination of the bond lengths clearly shows the partial double-bond character of S–C(5), N(1)–C(5), and N(2)–C(5). The possible hydrogen bonding in the structure (Fig. 2) and the partial conjugation of the heterocyclic ring show that the compound is more 2-amino than 2-imino, and that the structure of the ring is as shown in Fig. 4 (Amirthalingam & Muralidharan, 1969). The intramolecular S···O(1) distance is 2·96 Å and the angle C(3)–S···O is 65°. These values suggest a fairly strong S···O interaction (Lynch, Mel-

Table 2 (*cont.*)



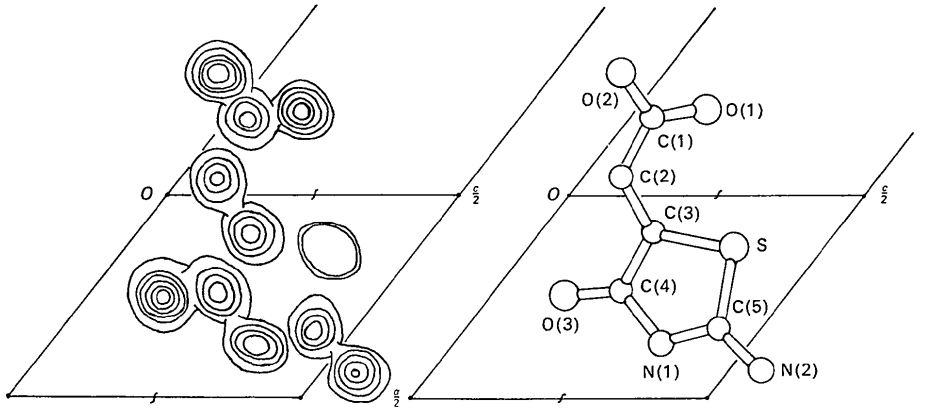


Fig. 1. Composite view of the molecule obtained from the final Fourier synthesis. Contours start from 1 e.Å^{-3} with intervals of 1 e.Å^{-3}, except for the sulphur atom where they are discontinued. Atoms are labelled as in the text.

lor & Nyburg, 1971) which also accounts for the partial conjugation of the heterocyclic ring (Johnson, Maier & Paul, 1970).

The molecules are linked by a system of O–H···N and N–H···O hydrogen bonds and by normal van der Waals forces (Table 3).

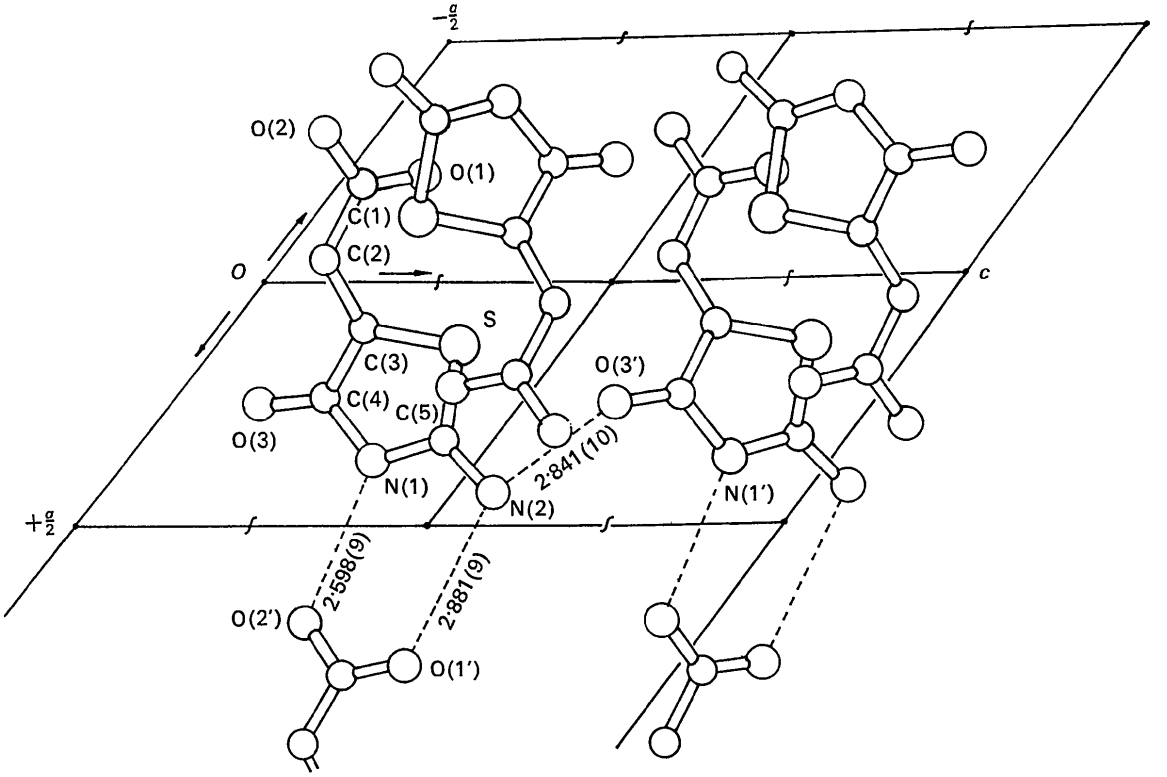


Fig. 2. Projection of the structure down **b**. Possible hydrogen bonds are shown by dotted lines.

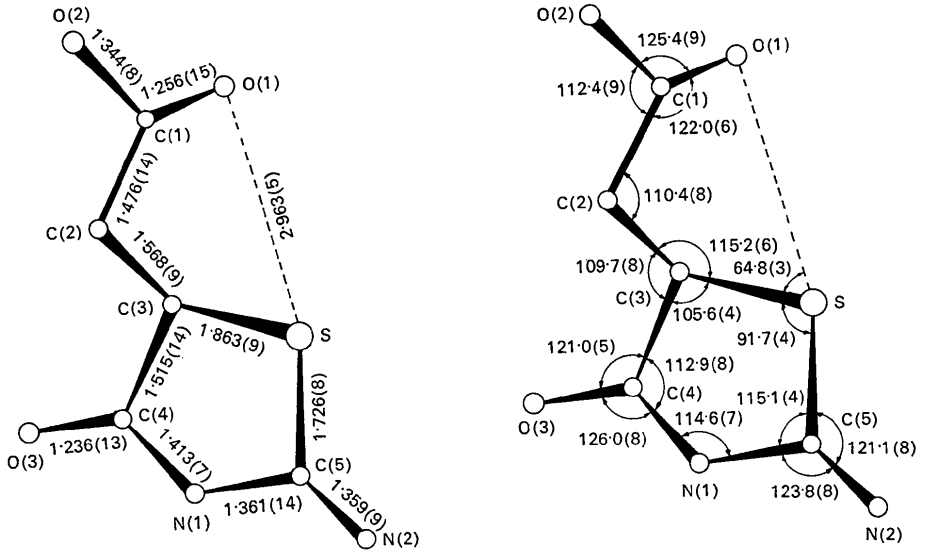


Fig. 3. Final bond lengths and angles with their standard deviations.

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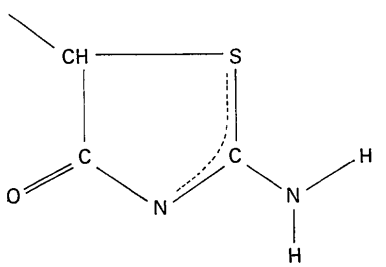

Fig. 4. Structure of the heterocyclic ring showing the partial conjugation.

Table 3. *Intermolecular contact distances shorter than 3·5 Å with e.s.d.'s in parentheses*

First designated atom of each pair belongs to the reference molecule and has the coordinates x,y,z listed in Table 1.

		Symmetry operation applied to 2nd atom
C(1)–N(1)	3·340 (9)	*A*
C(4)–O(2)	3·468 (9)	*B*
C(5)–O(3)	3·404 (14)	*C*
*N(1)–O(2)	2·598 (9)	*B*
*N(2)–O(1)	2·881 (9)	*B*
*N(2)–O(3)	2·841 (10)	*C*

Key to symmetry operations

A $1-x, \frac{1}{2}-y, \frac{1}{2}-z$
B $1+x, \frac{1}{2}-y, \frac{1}{2}+z$
C $x, \frac{1}{2}-y, \frac{1}{2}+z$

* Hydrogen bonds

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2-Imino-4-thiazolidinone, $C_3H_4N_2OS$, is monoclinic, space group $P2_1/n$, $Z=4$. The structure was solved by Patterson and minimum function methods with 467 visually estimated reflexions, and refined to $R=0{\cdot}115$. The molecule is planar. The bond lengths and the proposed hydrogen bonding in the crystal suggest that the heterocyclic ring exists almost as 2-imino with much less conjugation than the ring in 2-amino-4-thiazolidinone-5-acetic. acid.

Introduction

The structure analysis of 2-imino-4-thiazolidinone, $C_3H_4N_2OS$, has been undertaken to determine the amount of conjugation of the 5-membered ring compared with that in 2-amino-4-thiazolidinone-5-acetic acid (Amirthalingam & Muralidharan, 1972, hereafter referred to as A & M), and to discover whether the compound exists in the 2-amino or the 2-imino form.

Experimental

The crystals were colourless, monoclinic needles. The unit-cell parameters derived from Weissenberg photographs with Cu $K\alpha$ radiation ($\lambda=1{\cdot}542$ Å) are:

$a=4{\cdot}09$ (1), $b=9{\cdot}05$ (1), $c=13{\cdot}15$ (2) Å, $\beta=93{\cdot}0$ (5)°
$Z=4$, $d_o=1{\cdot}56$ g.cm^{-3}, $d_c=1{\cdot}59$ g.cm^{-3}.

The systematic absences $h0l$ with $h+l$ odd and $0k0$ with k odd characterize the space group uniquely as $P2_1/n$.

The reflexions nkl ($n=0$ to 2) and $h0l$ were recorded by the equi-inclination Weissenberg technique with Cu $K\alpha$ radiation and their intensities measured visually. The 467 unique reflexions were corrected for Lorentz and polarization effects and for spot size, but not for absorption. Initially the scaling of the nkl reflexions was done by Wilson plots.