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## Crystal and Molecular Structure of 1-Phenyl-4,5-(D-glucofurano)imidazolidine-2-thione

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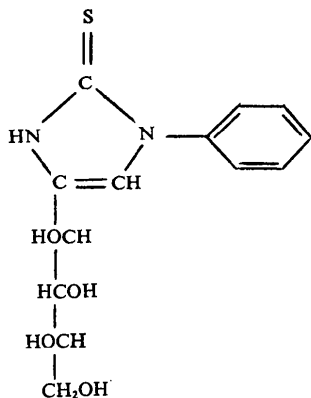
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The structure of the title compound,  $\text{SN}_2\text{O}_4\text{C}_{13}\text{H}_{16}$ , has been determined by single-crystal X-ray analysis from diffractometer data. The space group is  $P2_12_12_1$  with  $a=12.442$  (5),  $b=11.464$  (6),  $c=9.582$  (3) Å,  $Z=4$ . The structure was solved by direct methods and refined by full-matrix least-squares procedures to a final  $R$  of 0.041. The molecules are linked by van der Waals forces.

### Introduction

The crystal structure of 1-phenyl-4,5-(D-glucofurano)imidazolidine-2-thione has been determined as part of a research programme concerned with the conformational aspects of glucimidazols and C-nucleosides. For previous investigations in this series see listing in Conde, Moreno & Márquez (1975).

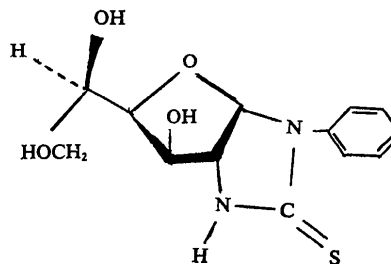
The compound given to us was originally formulated as 1-phenyl-4-(D-arabinotetrahydroxybutyl)imidazoline-2-thione.



This formula was established by NMR spectroscopy and oxidation analysis, but its molecular conformation could not be uniquely assigned and X-ray analysis was therefore suggested.

The structure determination reveals that the compound is consistent with the 1-phenyl-4,5-(D-glucofu-

rano)imidazolidine-2-thione conformation with the same empirical formula.



### Experimental

Single crystals of  $\text{SN}_2\text{O}_4\text{C}_{13}\text{H}_{16}$  were prepared and kindly supplied by Professor J. Fernández-Bolaños (Departamento de Química Orgánica of this University).

Preliminary rotation and Weissenberg photographs indicated orthorhombic symmetry. The only observed systematic absences were  $h00$  with  $h=2n+1$ ;  $0k0$  with  $k=2n+1$  and  $00l$  with  $l=2n+1$ , thus uniquely establishing the space group as  $P2_12_12_1$ .

The unit-cell parameters were determined by least-squares methods from 25 accurate  $2\theta$  values measured on an automatic four-circle diffractometer. The resulting values with other crystal data are:  $a=12.442$  (5),  $b=11.464$  (6),  $c=9.582$  (3) Å,  $V=1366.73$  Å<sup>3</sup>;  $M=296$ ;  $Z=4$ ;  $D_x=1.44$  g cm<sup>-3</sup>;  $F(000)=624$ .

Intensity data were collected by the  $\omega$ - $2\theta$  scan method on a Philips automated four-circle diffractom-

eter with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda=0.7107 \text{ \AA}$ ) to a maximum value of  $\sin \theta/\lambda=0.80$ . Three reflexions, monitored at regular intervals during data collection, showed no significant variation in intensity. The intensities of 2421 independent reflexions were measured. 1210 of these reflexions with  $I < 2\sigma(I)$  were considered as unobserved and assigned a zero weight throughout the refinement process. Data were corrected for Lorentz and polarization effects. No correction for absorption was applied ( $\mu R < 0.1$ ).

### Structure determination and refinement

Structure-factor amplitudes were placed on an absolute scale and normalized by using the scale factor and the overall temperature factor obtained from Wilson's (1942) statistics.

The structure was solved by direct methods using the program system developed by Germain, Main & Woolfson (1971). The set of phases with the highest figure of merit proved to give a sensible structure. A Fourier map was computed with this set of phases (177 reflexions with  $E > 1.40$ ). All the atoms except two appeared clearly in the map; these two were easily obtained from successive Fourier syntheses. The  $R$  value was 0.23. At this point a sequence of full-matrix least-squares refinement was begun, allowing for the simultaneous variation of coordinates, isotropic temperature factor and scale factor. After three cycles  $R$  was 0.10. Anisotropic temperature factors were then used in further refinement and  $R$  became 0.062. A full-matrix least-squares program written by Busing, Martin & Levy (1962) and a unit weighting scheme were employed. A difference Fourier synthesis calculated with  $\sin \theta$  up to 0.35 revealed the positions of the 16 hydrogen atoms. A further cycle of refinement

including the hydrogen atoms with isotropic temperature factors, and varying only the parameters of non-hydrogen atoms reduced  $R$  to 0.041. The shifts in the last cycle of refinement were less than  $0.1\sigma$  for all parameters. The correct enantiomorph was chosen in accord with the glucofurano ring configuration used in the preparation of the title compound. The atomic parameters from the final least-squares cycle are given in Table 1. The standard deviations were determined from the diagonal elements of the inverse matrix in the least-squares procedure. The atomic scattering factors for S, O, N and C atoms were those of Cromer & Mann (1968); that for the hydrogen atoms and  $\Delta f'$  and  $\Delta f''$  for the anomalous dispersion correction applied to the S atom were taken from *International Tables for X-ray Crystallography* (1962).\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31635 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

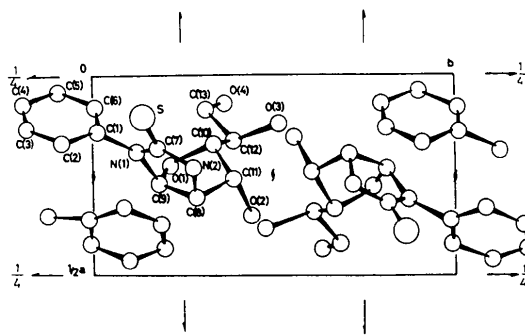


Fig. 1. Projection of the structure along the  $c$  axis.

Table 1. Atomic parameters

(a) Positional and anisotropic thermal parameters for non-hydrogen atoms with their estimated standard deviations ( $\times 10^4$ ). The expression used is  $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
S	1036 (1)	1380 (1)	5728 (2)	59 (1)	63 (1)	64 (2)	-7 (1)	6 (1)	-2 (1)
O(2)	3511 (3)	4353 (4)	1320 (5)	77 (3)	108 (4)	100 (6)	-41 (3)	16 (4)	18 (4)
O(1)	2200 (3)	2243 (3)	987 (4)	76 (3)	44 (2)	47 (5)	1 (2)	-1 (3)	1 (3)
O(3)	1262 (3)	5147 (3)	61 (5)	67 (3)	43 (2)	124 (6)	10 (2)	3 (3)	2 (3)
O(4)	635 (4)	3693 (4)	-2384 (5)	109 (4)	72 (3)	71 (6)	-11 (3)	-20 (4)	16 (4)
N(1)	1921 (3)	1258 (4)	3144 (5)	48 (2)	53 (3)	68 (6)	-1 (2)	6 (3)	5 (4)
N(2)	2367 (3)	2817 (4)	4311 (5)	59 (3)	67 (3)	67 (6)	-13 (3)	-10 (4)	4 (4)
C(1)	1475 (4)	150 (4)	2738 (6)	43 (3)	55 (4)	73 (7)	3 (3)	1 (4)	2 (4)
C(2)	1756 (4)	-846 (4)	3473 (7)	54 (3)	48 (4)	101 (9)	-1 (3)	-10 (5)	2 (5)
C(3)	1382 (5)	-1911 (5)	3025 (8)	59 (4)	68 (4)	140 (10)	8 (3)	0 (5)	0 (6)
C(4)	756 (5)	-1994 (5)	1828 (8)	66 (4)	63 (4)	124 (11)	-12 (3)	20 (5)	-33 (6)
C(5)	476 (5)	-994 (6)	1117 (8)	75 (4)	96 (6)	105 (10)	-30 (4)	-9 (5)	-14 (6)
C(6)	825 (5)	94 (5)	1588 (7)	68 (4)	80 (5)	82 (9)	-16 (4)	-24 (5)	19 (6)
C(7)	1790 (4)	1820 (4)	4370 (6)	49 (3)	54 (3)	61 (7)	5 (3)	-14 (4)	-5 (4)
C(8)	3001 (4)	2934 (4)	3086 (7)	60 (3)	58 (4)	62 (8)	-12 (3)	-2 (4)	10 (5)
C(9)	2685 (4)	1846 (4)	2214 (7)	51 (3)	57 (4)	83 (8)	-5 (3)	10 (4)	1 (5)
C(10)	2637 (4)	3972 (4)	2138 (7)	62 (3)	56 (4)	80 (8)	-18 (3)	10 (4)	7 (4)
C(11)	1793 (4)	3402 (4)	1222 (6)	52 (3)	42 (3)	68 (8)	-6 (3)	8 (4)	-4 (4)
C(12)	1566 (4)	3960 (4)	-167 (6)	63 (4)	48 (3)	81 (8)	2 (3)	-4 (4)	2 (4)
C(13)	731 (5)	3296 (5)	-979 (7)	77 (4)	65 (4)	78 (9)	-6 (4)	-6 (5)	5 (5)

Table 1 (cont.)

(b) Positional parameters for the hydrogen atoms

	x	y	z
H(C2)	0.225	-0.060	0.440
H(C3)	0.170	-0.260	0.353
H(C4)	0.040	-0.275	0.140
H(C5)	0.000	-0.125	0.020
H(C6)	0.060	0.075	0.080
H(N2)	0.250	0.325	0.520
H(C10)	0.235	0.460	0.270
H(C11)	0.105	0.335	0.180
H(C12)	0.232	0.395	-0.080
H(1) (C13)	0.005	0.350	-0.055
H(2) (C13)	0.100	0.250	-0.100
H(O2)	0.365	0.500	0.040
H(O3)	0.040	0.530	0.000
H(O4)	0.125	0.410	-0.265
H(C8)	0.380	0.300	0.320
H(C9)	0.335	0.132	0.210

## Results and discussion

The detailed conformation of the various rings in the molecule is defined by the torsion angles given in Table 4. Bond lengths and angles with the estimated standard deviations are given in Table 2. The average bond distances involving hydrogen atoms are: C-H = 1.05 (6), O-H = 1.06 (6) and N-H = 1.00 (5) Å. The mean aromatic C-C bond length is 1.38 Å and the mean angle 120°. The least-squares plane passing through the six benzene carbon atoms is given by equation (I) in Table 3. From this table it is seen that all six atoms are coplanar within the experimental deviation. The only substituent atom of the phenyl

Table 2. Bond distances (Å) and angles (°) with their standard deviations

(a) Bond lengths

S—C(7)	1.682 (6)	C(4)—C(3)	1.389 (10)
O(1)—C(9)	1.397 (7)	C(5)—C(4)	1.379 (9)
O(1)—C(11)	1.440 (6)	C(3)—C(2)	1.376 (8)
O(2)—C(10)	1.410 (7)	C(2)—C(1)	1.386 (7)
O(3)—C(12)	1.429 (6)	C(1)—C(6)	1.368 (8)
O(4)—C(13)	1.426 (8)	C(6)—C(5)	1.396 (9)
N(1)—C(1)	1.441 (6)	C(9)—C(8)	1.552 (8)
N(1)—C(9)	1.466 (7)	C(8)—C(10)	1.564 (8)
N(1)—C(7)	1.350 (7)	C(11)—C(10)	1.517 (8)
N(2)—C(8)	1.420 (8)	C(11)—C(12)	1.503 (8)
N(2)—C(7)	1.352 (7)	C(12)—C(13)	1.505 (8)

(b) Angles

C(1)—C(2)—C(3)	119.2 (5)	N(2)—C(8)—C(10)	113.0 (5)
C(2)—C(3)—C(4)	120.5 (6)	C(9)—C(8)—C(10)	103.0 (4)
C(3)—C(4)—C(5)	119.6 (6)	N(1)—C(9)—O(1)	112.4 (4)
C(4)—C(5)—C(6)	120.3 (6)	N(1)—C(9)—C(8)	101.9 (4)
C(5)—C(6)—C(1)	119.1 (6)	C(8)—C(9)—O(1)	107.5 (4)
C(6)—C(1)—C(2)	121.4 (5)	C(9)—O(1)—C(11)	108.7 (4)
N(1)—C(1)—C(2)	119.5 (5)	C(8)—C(10)—O(2)	109.6 (4)
N(1)—C(1)—C(6)	119.1 (5)	C(8)—C(10)—C(11)	102.0 (4)
C(7)—N(1)—C(9)	112.9 (4)	O(2)—C(10)—C(11)	110.2 (4)
C(1)—N(1)—C(7)	127.5 (4)	O(1)—C(11)—C(10)	104.1 (4)
C(1)—N(1)—C(9)	119.4 (4)	O(1)—C(11)—C(12)	108.7 (4)
S—C(7)—N(1)	126.7 (4)	C(10)—C(11)—C(12)	117.3 (4)
S—C(7)—N(2)	125.7 (4)	C(11)—C(12)—O(3)	108.6 (4)
N(1)—C(7)—N(2)	107.6 (4)	C(11)—C(12)—C(13)	111.9 (5)
C(7)—N(2)—C(8)	114.2 (4)	O(3)—C(12)—C(13)	112.2 (5)
N(2)—C(8)—C(9)	103.2 (4)	C(12)—C(13)—O(4)	112.6 (5)

Table 3. Least-squares planes in the molecule

(a) Equations of various planes in the standard orthogonal system as:  $Ax + By + Cz = D$ 

Plane	A	B	C	D
I Phenyl ring	0.8168	-0.0945	-0.5691	-0.0218
II Imidazolidine ring	0.7585	-0.5024	0.4150	2.3528
III Glucufurano ring	0.8140	0.0979	-0.5725	1.7595
IV O(1)—C(8)—C(9)—C(11)	0.8116	0.2487	-0.5286	2.2355

(b) Deviations in Å from the planes

	I	II	III	IV
S		0.108 *		
O(1)			0.179	0.126
O(2)			1.561	
N(1)	0.123*	-0.014	-1.397*	
N(2)		-0.027	-1.411*	
C(1)	0.011	0.042*		
C(2)	0.005			
C(3)	-0.015			
C(4)	0.010			
C(5)	0.005			
C(6)	-0.015			
C(7)		0.026		
C(8)		-0.017	-0.084	0.068
C(9)		0.002	-0.048	-0.120
C(10)			0.184	0.477*
C(11)			-0.232	-0.074
C(12)			0.363*	0.560*

\* Atom not included in calculation of the plane.

Table 4. Selected torsion angles (°)

N(1)—C(1)—C(2)—C(6)	3.6
C(2)—C(1)—N(1)—C(9)	68.2
C(1)—N(1)—C(9)—C(7)	4.8
S—C(7)—N(1)—N(2)	0.7
O(2)—C(11)—C(8)—C(10)	34.4
O(1)—C(9)—C(8)—C(11)	13.7
C(9)—C(8)—C(11)—C(10)	23.8
C(8)—C(11)—C(10)—O(1)	36.3
C(11)—C(10)—O(1)—C(9)	36.7
C(13)—C(12)—C(10)—O(1)	35.9
O(3)—C(12)—C(10)—O(1)	14.8
C(12)—C(10)—O(1)—C(9)	4.9
C(10)—O(1)—C(9)—C(8)	0.7
N(1)—C(9)—C(8)—C(11)	75.4
O(4)—C(13)—C(12)—C(10)	10.8
O(3)—C(12)—C(10)—C(13)	50.7
C(2)—C(1)—N(1)—C(7)	62.6
C(1)—N(1)—C(9)—C(8)	3.4
N(1)—C(9)—C(8)—O(1)	61.6

Table 5. Intermolecular distances less than 3.5 Å

S·····O(3 <sup>iv</sup> )	3.278 (7)
S·····O(4 <sup>iii</sup> )	3.248 (7)
O(4)····O(2 <sup>i</sup> )	2.773 (6)
C(2)····O(1 <sup>i</sup> )	3.171 (8)
C(8)····O(3 <sup>i</sup> )	3.043 (6)
C(3)····O(1 <sup>i</sup> )	3.363 (7)
C(11)····O(3 <sup>i</sup> )	3.277 (7)
C(11)····O(4 <sup>i</sup> )	3.464 (7)
C(4)····N(2 <sup>ii</sup> )	3.487 (7)
N(2)····O(3 <sup>i</sup> )	2.978 (4)

Symmetry code  
Superscript

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

Table 6. *Geometry of some intermolecular distances involving hydrogen*

A	B	A...B (Å)	A-H <sub>A</sub> (Å)	H <sub>A</sub> ...B (Å)	A...H <sub>B</sub> (Å)	H <sub>B</sub> -B (Å)	H <sub>A</sub> -A...B (°)	A-H <sub>A</sub> ...B (°)	A...H <sub>B</sub> -B (°)	H <sub>B</sub> -B...A (°)
O(4)...	O(2 <sup>1</sup> )	2.773 (6)	0.93 (6)	2.05 (6)	2.75 (5)	1.16 (6)	33 (3)	136 (6)	79 (3)	77 (3)
C(2)...	O(1 <sup>1</sup> )	3.171 (7)	1.11 (5)	2.52 (5)	-	-	45 (3)	116 (6)	-	-
C(8)...	O(3 <sup>1</sup> )	3.040 (7)	1.00 (6)	2.78 (6)	3.38 (6)	1.09 (6)	65 (3)	96 (6)	63 (3)	98 (3)

ring, N(1), is 0.12 Å from the plane. The C(1)-N(1) bond of 1.44 Å agrees with the C-N (1.44 Å) distance given by Aupers, Carlisle & Lindley (1974) and the C-N (1.45 Å) reported for bromophenyl-4,5-(D-glucofurano)imidazolidine-2-thione by Vega, Hernández-Montis & López-Castro (1976).

The bond lengths and angles in the glucofurano-imidazolidine ring agree well with the corresponding parameters from the other analogous compounds. The S-C(7), C(7)-N(1) and C(7)-N(2) distances indicate the effect of the thiourea resonance system (Valle, Cojazzi, Busetti & Mammi, 1970; Jiménez-Garay, López-Castro & Márquez, 1974; Conde, Moreno & Márquez, 1975).

The N(1)-C(9) bond (1.47 Å) is equal to the accepted N-C single bond of 1.47 Å and agrees with the N-C (1.46 Å) distance found by Jiménez-Garay, López-Castro & Márquez (1974) in 1-methyl-4,5-(D-glucofurano)imidazolidine-2-thione. The C(8)-C(9) bond length of 1.55 Å agrees with the values reported for the C-C single bond. The imidazolidine ring is planar as expected. The least-squares plane calculated for the five atoms of the ring is given by equation (II) (Table 3). The S and C(1) atoms were not included in this best-plane calculation through the imidazolidine ring and these atoms lie respectively +0.11 and +0.04 Å from it. There is discrepancy between the C(9)-O(1) and O(1)-C(11) distances of 1.40 and 1.44 Å. As found in analogous compounds, this may be due to the anomeric effect (Berman, Chu & Jeffrey, 1967; Conde, Moreno & Márquez, 1975). The C-C-C, C-C-O and C-O-C angles in the glucofurano ring have average values of 103, 106 and 109° respectively and are comparable with those of Rahman & Wilson (1972) and Jiménez-Garay, López-Castro & Márquez (1974).

The glucofurano ring exists in the envelope conformation. The C(10) atom is displaced by 0.48 Å from the least-squares plane defined by the atoms O(1), C(9), C(8) and C(11) and is situated on the same side of this plane as C(12) (Table 3). The exocyclic lengths and angles are normal.

The dihedral angles between the mean planes of the phenyl and imidazolidine rings and the glucofurano-imidazolidine ring are 85 and 103° respectively.

Fig. 1 shows a view of the arrangement of mole-

cules in the unit cell along [001]. The molecules are intimately stacked through van der Waals forces. Table 5 lists intermolecular distances less than 3.5 Å. The geometry of some relevant intermolecular distances involving hydrogen atoms is given in Table 6. From this table may be derived a possible weak hydrogen bond O(4)-H...O(2).

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Computations were carried out on a DCT 2000 terminal of the Computing Centre of this University, connected to a Univac 1108.

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