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The Crystal and Molecular Structure of 1-*p*-Tolyl-4-(α-D-erythrofuranosyl)imidazoline-2-thione

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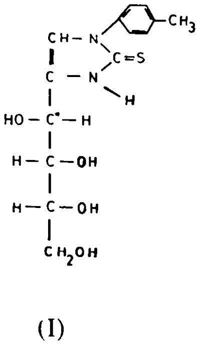
The structure of the title compound $SN_2O_3C_{14}H_{16}$ has been determined by single-crystal X-ray analysis from diffractometer data. The space group is $P2_12_12_1$ with $a = 29{\cdot}586$ (15), $b = 7{\cdot}714$ (5), $c = 5{\cdot}898$ (3) Å, $Z = 4$. The structure was solved by direct methods and refined by full-matrix least-squares procedures to a final R of 0·074. The molecules are linked together by hydrogen bonds and van der Waals forces.

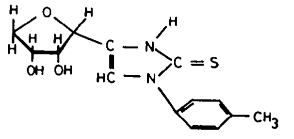
Introduction

The crystal structure of 1-*p*-tolyl-4-(α-D-erythrofuranosyl)imidazoline-2-thione has been determined as part of a continuing investigation in this laboratory of the conformational aspects of imidazole *C*-nucleosides which can be obtained by dehydration of polyhydroxyalkylimidazoles. For previous investigations in this series see the listing in Vega, Hernández-Montis & López-Castro (1976), and the papers by Jiménez-Garay, López-Castro & Márquez (1976) and Jiménez-Garay, Vega & López-Castro (1976).

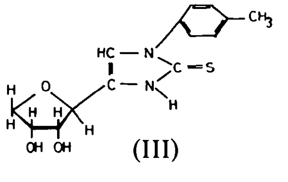
The title compound (II) has been obtained by dehydration of 1-*p*-tolyl-4-(D-arabinotetrahydroxybutyl)-imidazoline-3-thione (I), refluxing in trifluoroacetic acid. The dehydration takes place between hydroxyls 1 and 4 of the chain, with retention of configuration at C(1). The β anomer (III), with inversion at C(1), has been obtained by heating under pressure an aqueous solution of I.



(I)



(II)



(III)

The two anomers (II, III) have the empirical formula $SN_2O_3C_{14}H_{16}$ and different melting points and optical rotations. This paper corresponds to the structure determination of the α anomer. A three-dimensional X-ray analysis shows that the structure corresponds to the formula II.

Experimental

Crystals of 1-*p*-tolyl-4-(α-D-erythrofuranosyl)imidazoline-2-thione are colourless prisms, elongated along **c**. The crystal data are: $a = 29{\cdot}586$ (15), $b = 7{\cdot}714$ (5), $c = 5{\cdot}898$ (3) Å, $V = 1340{\cdot}18$ Å^3, $Z = 4$, $D_m = 1{\cdot}48$, $D_c = 1{\cdot}45$ g cm^{-3}, $F(000) = 616$, $\mu(\text{Mo } K\alpha) = 2{\cdot}478$ cm^{-1}. Space group $P2_12_12_1$ (from systematic absences). Preliminary rotation and Weissenberg photography were used to determine the space group and approximate unit-cell dimensions; more accurate values were calculated by a least-squares treatment of $(\theta,\chi,\varphi)_{hkl}$ angles measured on an automated diffractometer for 25 reflexions.

Intensity data were collected by the ω–2θ scan method on a Philips automated four-circle diffractometer with graphite-monochromated, Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). Reflexions were collected to a maximum value of $\sin\theta/\lambda = 0{\cdot}60$. Three reference reflexions were measured after every 50 reflexions during the data collection. The variation in intensity was observed to be less than 2% of its mean value.

The intensities of 2292 independent reflexions were measured. Of these, 1281 with $I < 2\sigma(I)$ were considered as unobserved and were assigned a zero weight throughout the refinement process. The data were corrected for Lorentz–polarization effects but not for absorption ($\mu R < 0{\cdot}1$).

Structure determination and refinement

The observed structure factors were converted into normalized structure amplitudes, $|E|$, by using the scale factor and the overall temperature factor obtained from Wilson statistics. The $|E|$ statistics indicated a non-centrosymmetric structure consistent with the space group determined from systematic absences.

The structure was solved by multisolution tangent formula refinement (Germain, Main & Woolfson,

1971) of 320 reflexions with $E > 1·40$. An E map calculated from the set with the highest figure of merit gave 13 atoms of the structure. R was 0·39. The remaining non-hydrogen atoms were located from a three-dimensional electron-density synthesis in which the phase angles were determined from the known atomic positions. An isotropic temperature factor $\exp(-B \sin^2 \theta/\lambda^2)$ with $B = 2·5$ Å^2 was used in calculating structure factors and the R value was 0·24. After two cycles of Fourier syntheses and structure factor calculations, the R value dropped to 0·15.

The whole structure, excluding H atoms, was then refined with full-matrix least-squares methods varying all positional parameters and temperature factors. Six cycles, of which the last three were with anisotropic thermal factors, were sufficient to reduce the discrepancy index to 0·089. A full-matrix least-squares program written by Busing, Martin & Levy (1964) was used and a weighting function $\omega = 1/\sigma^2$ gave the best results.

Table 1. *Atomic coordinates* ($\times 10^4$) *for non-hydrogen atoms*

	x	y	z
O(1)	2177 (2)	−2095 (9)	−685 (11)
O(2)	2452 (2)	−2241 (9)	−6177 (11)
O(3)	1932 (3)	191 (9)	−4440 (13)
N(1)	1034 (2)	1031 (10)	2083 (13)
N(2)	1627 (3)	1285 (10)	−47 (14)
C(1)	−469 (4)	2091 (15)	7974 (20)
C(2)	659 (3)	1351 (13)	3564 (17)
C(3)	729 (4)	2137 (13)	5616 (18)
C(4)	364 (4)	2396 (13)	7034 (20)
C(5)	−66 (4)	1836 (13)	6455 (19)
C(6)	−134 (3)	1060 (12)	4337 (18)
C(7)	234 (3)	813 (14)	2911 (20)
C(8)	1345 (4)	2197 (13)	1317 (17)
C(9)	1126 (3)	−603 (13)	1172 (15)
C(10)	1492 (3)	−433 (13)	−93 (16)
C(11)	1714 (3)	−1834 (13)	−1429 (16)
C(12)	1761 (4)	−1542 (14)	−3991 (18)
C(13)	2136 (4)	−2906 (13)	−4604 (20)
C(14)	2372 (4)	−3305 (14)	−2311 (16)
S	1366 (1)	4344 (3)	1796 (6)

Table 2. *Atomic coordinates* ($\times 10^3$) *and isotropic temperature factors for the hydrogen atoms*

	x	y	z	B (Å^2)
H1(C1)	−80	222	780	3·4
H2(C1)	−39	119	880	3·4
H3(C1)	−35	280	940	3·4
H(C3)	85	240	740	2·8
H(C4)	45	300	870	3·0
H(C6)	−48	62	405	2·5
H(C7)	19	6	126	2·7
H(N2)	187	186	−6	2·4
H(C9)	90	−160	170	2·1
H(C11)	154	−300	−108	2·1
H(C12)	145	−150	−510	2·6
H(C13)	197	−422	−500	2·8
H1(C14)	225	−455	−160	3·1
H2(C14)	266	−298	−220	3·1
H(O2)	263	−203	−780	2·9
H(O3)	223	20	−480	3·4

Difference Fourier syntheses calculated with $\sin \theta$ up to 0·35 revealed 16 H atoms in stereochemically feasible positions. The H atoms were assigned isotropic temperature factors equal to those of the atoms bonded to them for subsequent structure calculations. After two further cycles of least-squares calculations for the non-hydrogen atomic parameters, refinement was terminated with $R = 0·074$. The shifts in the last cycle of refinement were less than σ for all parameters. The correct enantiomorph was chosen in accord with the configuration of the sugar used in the preparation of the title compound. The atomic parameters from the final least-squares cycle are given in Tables 1 and 2.† The standard deviations were determined from the diagonal elements of the inverse matrix in the least-squares procedure.

Table 3. *Least-squares planes in the molecule*

(*a*) Equations of various planes in the orthogonal system, in the form: $Ax + By + Cz = D$

		A	B	C	D
(I)	Phenyl ring	−0·1711	0·8927	−0·4170	−0·2759
(II)	Imidazoline ring	0·5813	−0·2020	0·7882	2·5818
(III)	Furanosyl ring	0·5383	0·8331	−0·1267	1·9294

(*b*) Deviations (Å) from the planes

	(I)	(II)	(III)
S		−0·074*	
N(1)	−0·050*	0·004	
N(2)		−0·005	
C(1)	−0·008*		
C(2)	−0·004	−0·003*	
C(3)	−0·003		
C(4)	0·011		
C(5)	−0·014		
C(6)	0·007		
C(7)	0·001		
C(8)		0·001	
C(9)		−0·007	
C(10)		0·008	0·176*
C(11)		−0·012*	0·271
C(12)			0·183
C(13)			−0·051
C(14)			−0·104
O(1)			0·242
O(2)			0·998*
O(3)			1·603*

* Atoms not included when calculating the plane.

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32458 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The atomic scattering factors used were taken from Cromer & Mann (1968) for S, O, N and C atoms, and from *International Tables for X-ray Crystallography* (1962) for H.

Results and discussion

(i) *Planarity in the molecule*

The planes of best fit for the rings in the molecule and their atomic displacements are listed in Table 3. Both the phenyl and the imidazoline rings are planar with mean atomic displacements of 0·007 and 0·004 Å, respectively. The dihedral angle between the phenyl and imidazoline rings is 53°, which indicates, according to the theory of Kitaigorodsky (1965), that the most important term in the conformational energy is the potential energy. In substances such as these the energies involved in determining the conformation are the potential energy, the resonance energy and the lattice energy. The first term reaches a minimum when the phenyl ring is perpendicular to the imidazoline ring, while the other two terms attain minima when the two rings are coplanar.

The glucofuran rings are not planar, as expected. The dihedral angle of 87° between the imidazoline and sugar rings shows also that the potential energy terms predominate largely.

The C(10), O(2) and O(3) atoms bonded to the glucofuran ring deviate to the same side of the mean plane through the ring; therefore, this corresponds to an α-configuration of the group.

(ii) *Molecular dimensions*

Bond lengths and angles in the molecule with estimated standard deviations are listed in Tables 4 and 5. Fig. 1 shows a labelled perspective drawing of the molecule in the cell.

The averages of the bond lengths and angles in the phenyl ring, 1·39 Å and 120°, are within the expected ranges. The C(1) atom is practically in the plane of the phenyl ring and the C(1)–C(5) distance of 1·50 Å, although shorter than the corresponding C–C (phenyl) length of 1·52 Å, is consistent with the C–C (phenyl) = 1·51 Å reported by Kaftory & Dunitz (1975). The inter-ring distance C(2)–N(1) of 1·43 Å agrees with the single bond N–C (phenyl) found in analogous compounds (Pérez-Garrido, Conde & Márquez, 1974; Conde, Moreno & Márquez, 1975).

The observed value of 1·68 Å for the bond length S–C(8) is intermediate between the S–C single-bond distance of 1·81 Å and the double-bond value of 1·56 Å. This partial double-bond character is in agreement with the canonical resonance forms of the thiourea system and is a normal feature of these compounds (Valle, Cojazzi, Bussetti & Mammi, 1970; Pérez-Garrido, López-Castro & Márquez, 1973; Jiménez-Garay, López-Castro & Márquez, 1974). The bond distances and angles in the imidazoline ring, excluding C(9)–C(10), are in agreement with the values reported in the literature. The C(9)–C(10) distance of 1·32 Å is rather short.

The inter-ring bond C(10)–C(11) is normal. In the sugar ring the values of the bond lengths and angles are

Table 4. *Bond lengths* (Å)

O(1)–C(11)	1·45 (1)	C(1)–C(7)	1·38 (1)
O(1)–C(14)	1·46 (1)	C(3)–C(4)	1·38 (2)
O(2)–C(13)	1·41 (1)	C(4)–C(5)	1·39 (1)
O(3)–C(12)	1·45 (1)	C(5)–C(6)	1·40 (1)
N(1)–C(2)	1·43 (1)	C(6)–C(7)	1·39 (1)
N(1)–C(8)	1·36 (1)	C(8)–S	1·68 (1)
N(1)–C(9)	1·40 (1)	C(9)–C(10)	1·32 (1)
N(2)–C(8)	1·36 (1)	C(10)–C(11)	1·49 (1)
N(2)–C(10)	1·39 (1)	C(11)–C(12)	1·53 (1)
C(1)–C(5)	1·50 (1)	C(12)–C(13)	1·57 (1)
C(2)–C(3)	1·37 (1)	C(13)–C(14)	1·55 (1)

Table 5. *Bond angles* (°)

C(11)–O(1)–C(14)	102·0 (7)	N(2)–C(8)–S	128·2 (8)
C(2)–N(1)–C(8)	124·2 (8)	N(1)–C(8)–N(2)	101·5 (8)
C(2)–N(1)–C(9)	123·1 (8)	N(1)–C(9)–C(10)	105·9 (8)
C(8)–N(1)–C(9)	112·7 (8)	N(2)–C(10)–C(11)	128·5 (8)
C(8)–N(2)–C(10)	112·8 (8)	C(9)–C(10)–C(11)	124·3 (9)
N(1)–C(2)–C(3)	124·1 (9)	N(2)–C(10)–C(9)	107·2 (9)
N(1)–C(2)–C(7)	113·1 (9)	O(1)–C(11)–C(10)	107·7 (8)
C(3)–C(2)–C(7)	122·8 (10)	O(1)–C(11)–C(12)	106·3 (8)
C(2)–C(3)–C(4)	122·9 (10)	C(10)–C(11)–C(12)	117·1 (8)
C(3)–C(4)–C(5)	116·0 (10)	O(3)–C(12)–C(13)	114·1 (8)
C(1)–C(5)–C(4)	117·1 (10)	O(3)–C(12)–C(11)	110·1 (8)
C(1)–C(5)–C(6)	122·5 (9)	C(11)–C(12)–C(13)	100·9 (8)
C(4)–C(5)–C(6)	120·4 (10)	O(2)–C(13)–C(12)	107·8 (8)
C(5)–C(6)–C(7)	123·3 (10)	C(12)–C(13)–C(14)	101·3 (8)
C(2)–C(7)–C(6)	114·5 (10)	O(2)–C(13)–C(14)	116·2 (9)
N(1)–C(8)–S	130·3 (8)	O(1)–C(14)–C(13)	108·6 (8)

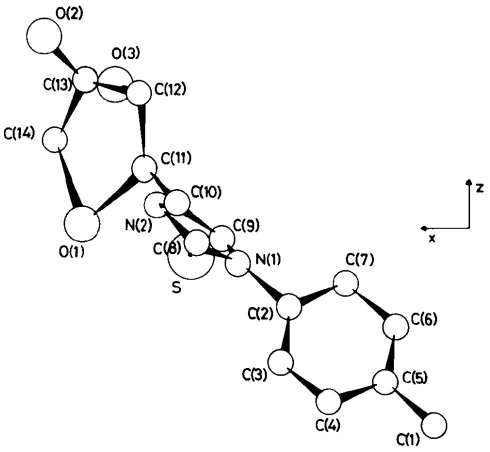

Fig. 1. A perspective view of the molecule.

Table 6. *Geometry of intermolecular contacts less than the sum of the van der Waals radii*

Symmetry code: (i) $\frac{1}{2} - x, -y, \frac{1}{2} + z$.

A	B	t	$A \cdots B$	A–H$_A$	B–H$_B$
O(1)···	O(2)	(001)	2·78 (1) Å		1·10 (8) Å
O(2)···	N(2$^{\text{i}}$)	(00$\bar{1}$)	2·90 (1)	1·10 (8) Å	0·90 (12)
C(9)···	C(12)	(00$\bar{1}$)	3·49 (1)	1·07 (10)	1·13 (12)

A	B	t	A–H$_A \cdots B$	$A \cdots$H$_B$–B	H$_A$–$A \cdots B$	H$_B$–$B \cdots A$	H$_A \cdots B \cdots A$	H$_B \cdots A \cdots B$
O(1)···	O(2)	(001)		113 (6)°		46 (5)°		22 (2)°
O(2)···	N(2$^{\text{i}}$)	(00$\bar{1}$)	84 (5)°	155 (8)	73 (5)°	18 (2)	22 (2)°	8 (2)
C(9)···	C(12)	(001)	76 (5)	146 (6)	87 (5)	23 (5)	17 (1)	10 (2)

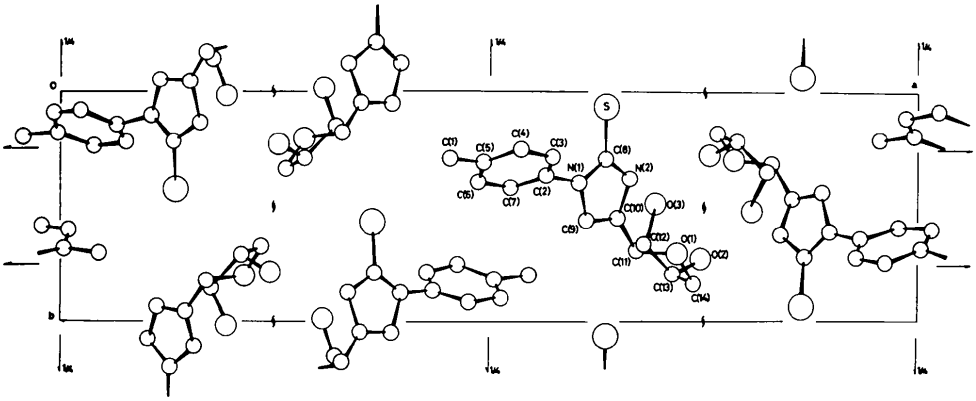

Fig. 2. Projection of the structure along **c**.

Table 7. *Torsion angles* (°)

O(1)–C(11)–C(10)–C(9)	−120·0 (10)
C(14)–O(1)–C(11)–C(12)	−46·1 (8)
O(1)–C(11)–C(12)–C(13)	39·7 (7)
C(11)–C(12)–C(13)–C(14)	−19·7 (9)
C(12)–C(13)–C(14)–O(1)	−6·5 (9)
C(13)–C(14)–O(1)–C(11)	32·4 (8)
C(1)–C(5)–C(4)–C(6)	−177·6 (9)
N(1)–C(2)–C(3)–C(7)	−178·1 (8)
O(2)–C(13)–C(14)–O(1)	114·1 (7)
O(3)–C(12)–C(11)–O(1)	−75·6 (9)
S–C(8)–N(1)–C(2)	−2·7 (12)
S–C(8)–N(2)–C(10)	−177·3 (7)
S–C(8)–N(1)–C(9)	176·3 (6)
O(3)–C(12)–C(13)–C(14)	96·5 (7)
O(2)–C(13)–C(12)–C(11)	−139·1 (7)

in agreement with the values reported. The mean C—H distance is 1·05 (9) Å.

The conformation of the molecule is characterized by the valency angles (Table 5) and the torsional angles of the individual bonds, which are given in Table 7.

Intermolecular contacts are listed in Table 6.

(iii) *Molecular packing*

Fig. 2 shows a view of the arrangement of the molecules in the unit cell as viewed along [001]. The molecular packing is clearly dominated by the formation of hydrogen bonds and van der Waals forces. Each molecule of 1-*p*-tolyl-4-(α-D-erythrofuranosyl)-imidazoline-2-thione is connected to the neighbouring molecules. The details of the molecular interactions are given in Table 6, which contains those intermolecular contacts which are less than the sum of the van der Waals radii (Pauling, 1966). There is only one intermolecular hydrogen bond, O(2)···H—N(2) of 2·90 Å, between atoms of molecules related by twofold screw axes and a −**c** translation. There are two intermolecular van der Waals interactions, O(1)···O(2) of 2·78 Å and C(9)···C(12) of 3·49 Å, both between atoms of molecules related by a translation along **c**. The result is the production of a helical system along **c**.

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The Crystal Structure of the *epi*-Inositol–Strontium Chloride Complex

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The crystal structure of the *epi*-inositol–strontium chloride complex, $C_6H_{12}O_6.SrCl_2.5H_2O$, has been determined by a three-dimensional X-ray analysis. The space group is $P2_12_12_1$, with $Z = 4$, $a = 13{\cdot}561\ (5)$, $b = 15{\cdot}763\ (5)$, $c = 7{\cdot}364\ (5)$ Å. Structure determination was by the Patterson method, and full-matrix least-squares refinement of the positional and thermal parameters yielded a final unweighted R value of 0·020. The Sr ion is coordinated, with a mean Sr···O distance of 2·63 (5) Å, to nine O atoms, three of the oxygens being from the axial–equatorial–axial sequence of hydroxyls in the *epi*-inositol molecule. The position of the Sr ion in relation to these ax.–eq.–ax. oxygens confirms the structure of the complex postulated from NMR results.

Introduction

Mills (1961) (using paper ionophoresis) found that *epi*-inositol, in supporting electrolytes containing acetates of the alkali and alkaline-earth metals, revealed considerable movement towards the cathode. This was interpreted as being due to the formation of a complex with the cation. The crystal structure of *epi*-inositol has been determined by Jeffrey & Kim (1971), and this study showed the presence of an axial–equatorial–axial sequence of three hydroxyl groups in the molecule. It was proposed by Angyal & Davies (1971) that the ax.–eq.–ax. sequence was the site of complex formation. Subsequent observation of the NMR spectra of various *epi*-inositol complexes with cations (Angyal & Hickman, 1975) tended to confirm this proposal; it was to verify the NMR results that the X-ray study of the *epi*-inositol–strontium chloride complex was carried out.

Experimental

Colourless, striated, needle-shaped crystals were obtained by crystallization of the complex from aqueous methanol (Angyal & Hickman, 1975). Because of the striations, the crystal was 'rounded' in a crystal spherizer to an approximately cylindrical shape of diameter 0·37 mm and length 0·41 mm.

The space group was determined from zero- and first-level Weissenberg photographs about **a** and **c** with Ni-filtered Cu $K\alpha$ radiation. The absence of reflexions