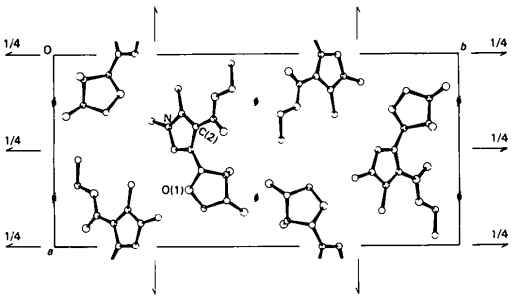

Fig. 2. A view along [001] of the unit-cell contents.

The authors thank Professor Fernández-Bolaños for supplying the crystals. The present work is part of a wider research project supported by the Government through the 'Comisión Asesora de Investigación Científica y Técnica'.

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Structure of 4-(β-D-Erythrofuranosyl)-3-methyl-1-(*p*-tolyl)-4-imidazoline-2-thione Monohydrate, $C_{15}H_{18}N_2O_3S.H_2O$

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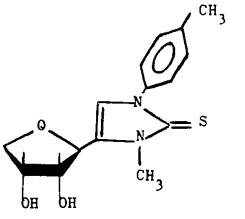
(*Received* 1 *June* 1982; *accepted* 5 *October* 1982)

Abstract. $M_r = 324{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 32{\cdot}150\ (5)$, $b = 10{\cdot}215\ (1)$, $c = 4{\cdot}805\ (1)$ Å, $V = 1578{\cdot}0\ (4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}36$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 1{\cdot}953$ mm^{-1}, $T = 300$ K, final $R = 0{\cdot}050$ for 1361 observed $[I > 2\sigma(I)]$ independent reflexions. The sugar ring adopts a conformation intermediate between envelope ^2E and twist ^2_1T forms. The orientation of the imidazoline ring with respect to the furanose is *anti*; the glycosidic angle is 24·6 (7)°. The crystal packing is due to hydrogen bonds involving the hydration water molecules.

Introduction. Heterocyclic *C*-nucleosides are interesting because of their structural analogies with natural *C*-nucleosides and because of their antiviral activity (Hanessian & Pernet, 1976).

Potential anticancer and radioprotective characteristics were reported (Weitzel, Schneider, Guglielmi, Sander, Durst & Hirschmann, 1966) for imidazole *C*-nucleosides.

The crystal structure of the title compound has been determined as part of a systematic structural investigation of imidazole *C*-nucleosides synthesized (Fernández-Bolaños, Fuentes-Mota, Barragán Peréz & Pradera de Fuentes, 1978) in the Organic Chemistry Department of this University.



(I)

The title compound (I) was obtained (Fernández-Bolaños, Fuentes-Mota & Fernández-Bolaños Guzmán, 1982) by the catalyzed formation of the anhydride of 3-methyl-4-(D-*arabino*-1,2,3,4-tetrahydroxybutyl)-1-(*p*-tolyl)-4-imidazoline-2-thione and it is the first disubstituted (at both atoms) imidazole *C*-nucleoside.

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Experimental. Needle-shaped colorless crystals kindly supplied by Professor Fernández-Bolaños of the Organic Chemistry Department of this University; preliminary studies indicated orthorhombic symmetry, systematic absences consistent with $P2_12_12_1$; Philips PW 1100 four-circle computer-controlled diffractometer, graphite-monochromated radiation, unit-cell parameters obtained from least-squares refinement of the θ values of 31 reflexions, 1728 reflexions measured with $\theta<68°$ ($h<39$, $k<13$, $l<6$), ω–2θ scan mode, 1361 with $I>2\sigma(I)$ considered observed; two reflexions monitored periodically, changes in intensity <2%; Lorentz and polarization corrections, no absorption or extinction corrections; weighted tangent-formula refinement (*MULTAN* 78: Main, Lessinger, Hull, Germain, Declercq & Woolfson, 1978) of 180 reflexions with $|E|>1.20$; the E map performed with the phase set showing the highest figure of merit and a further Fourier synthesis revealed the positions of all the non-hydrogen atoms; full-matrix least-squares refinement of 260 parameters over all observed reflexions based on F_o [*CRYLSQ* of the XRAY system (Stewart, Kundell & Baldwin, 1970)] followed by a Fourier difference synthesis up to sin $\theta/\lambda = 0.7$ Å^{-1} revealed the H-atom positions; a final least-squares process in a mixed mode including H atoms (with isotropic temperature factors equal to those of the attached atoms) gave $wR = 0.049$;* the final average ratio of shift to error was 0.5 and the maximum was 1.1; $F(000) = 688$; scattering factors from *International Tables for X-ray Crystallography* (1974); the weighting scheme was based on counting statistics.

Discussion. Final atomic coordinates and isotropic thermal parameters are given in Table 1. Bond lengths and angles for the non-hydrogen atoms together with their estimated standard deviations are given in Fig.1. The C–H distances range from 0.88 to 1.14 Å, with an average value of 1.07 (2) Å. The average O–H bond length is 0.92 (7) Å.

Imidazoline ring. Bond distances and angles in the imidazoline ring agree quite well with the mean values reported for analogous imidazoline-2-thione compounds (Conde, López-Castro & Márquez, 1978). The partial double-bond character of the S–C bond is in agreement with the canonical resonance forms of the thiourea system and is a normal feature of these compounds. The ring is planar and the atomic deviations from the least-squares plane are within the standard deviations.

The phenyl ring, planar as expected, and with an average C–C bond length of 1.391 (3) Å and C–C–C

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38160 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^5$, *for* H $\times 10^3$) *and isotropic thermal parameters* ($\times 10^4$, *for* H $\times 10^3$)

For non-hydrogen atoms $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j \cos(\mathbf{a}_i,\mathbf{a}_j)$.

	x	y	z	U_{eq}/U(Å^2)
S	11161 (4)	89890 (12)	48458 (41)	498 (8)
O(1)	12586 (10)	32667 (33)	91632 (102)	542 (16)
O(2)	3656 (12)	22879 (36)	109617 (82)	469 (14)
O(3)	2229 (10)	40718 (37)	68782 (80)	461 (14)
O(4)	1833 (10)	98003 (34)	30365 (87)	471 (14)
N(1)	15161 (11)	66112 (38)	43502 (110)	407 (16)
N(2)	9627 (11)	65748 (38)	70119 (108)	388 (16)
C(1)	11970 (14)	73789 (48)	53380 (136)	402 (18)
C(2)	14713 (15)	53398 (47)	53799 (148)	453 (20)
C(3)	11348 (15)	53151 (46)	70443 (131)	400 (18)
C(4)	9417 (15)	42072 (46)	86577 (124)	386 (18)
C(5)	10703 (17)	19825 (49)	92847 (166)	581 (23)
C(6)	6158 (17)	21321 (53)	85723 (129)	444 (20)
C(7)	6129 (15)	34390 (52)	70348 (125)	408 (18)
C(8)	18757 (14)	70430 (47)	28673 (123)	383 (18)
C(9)	18430 (16)	79441 (54)	7382 (134)	487 (20)
C(10)	22036 (17)	83731 (55)	−5969 (146)	551 (22)
C(11)	25967 (16)	79045 (53)	2069 (145)	508 (21)
C(12)	26112 (16)	69837 (56)	23165 (138)	498 (21)
C(13)	22585 (15)	65466 (51)	36787 (136)	463 (20)
C(14)	29805 (22)	84001 (78)	−12078 (183)	717 (29)
C(15)	5929 (20)	70243 (76)	84814 (170)	553 (22)
H(O2)	25 (2)	157 (6)	1187 (16)	61
H(O3)	10 (2)	418 (6)	864 (14)	56
H(2)	168 (2)	459 (6)	497 (16)	53
H(4)	82 (2)	460 (6)	1068 (15)	49
H(6)	49 (2)	128 (6)	734 (15)	54
H(7)	72 (2)	342 (6)	482 (15)	47
H(9)	153 (2)	833 (6)	1 (17)	64
H(10)	217 (2)	910 (7)	−236 (15)	67
H(12)	291 (2)	670 (6)	275 (16)	61
H(13)	231 (2)	592 (6)	549 (15)	58
H(15)	119 (2)	147 (8)	1114 (16)	69
H(25)	122 (2)	146 (8)	792 (16)	69
H(104)	8 (2)	952 (6)	145 (15)	58
H(114)	294 (2)	897 (8)	−278 (18)	81
H(115)	57 (2)	810 (7)	882 (16)	60
H(204)	46 (2)	954 (6)	355 (15)	58
H(214)	317 (2)	895 (8)	34 (19)	81
H(215)	33 (2)	664 (7)	775 (17)	60
H(314)	317 (2)	780 (8)	−190 (19)	81
H(315)	62 (2)	691 (8)	1034 (18)	60

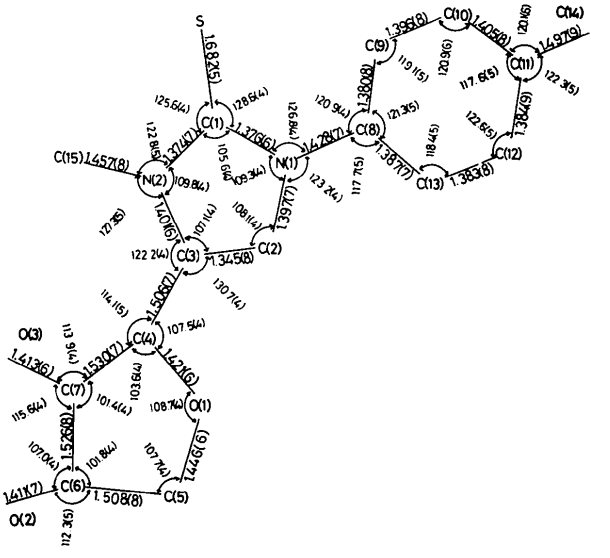

Fig. 1. Bond lengths (Å) and angles (°).

angle of 120·0 (2)°, forms a dihedral angle of 40·7 (2)° with the imidazoline ring.

This value is lower than those observed in the compounds studied previously, in which the dihedral angle ranges from 60 to 80°, indicating a more significant contribution of crystal forces to the phenyl–imidazoline subrotation.

Furanosyl ring. Bond lengths and angles in the sugar ring agree quite well with mean values reported for these compounds. The asymmetry of the endocyclic bonds O(1)–C(4) = 1·421 (6) and O(1)–C(5) = 1·446 (6) Å may be due to anomeric effects.

Average values for the C–C–C, C–C–O and C–O–C endocyclic angles of 101·6 (4). 105·6 (4) and 108·7 (4)° agree with the mean values reported (Conde, López-Castro & Márquez, 1978). The furanosyl ring is not planar, as shown by the deviations from the least-squares plane (Table 2) through the five atoms of the ring. In terms of ring-puckering coordinates (Cremer & Pople, 1975) the amplitude phase magnitudes are $q = 0{\cdot}40\ (1)$ Å and $\varphi = 66{\cdot}6\ (5)°$ for the sequence O(1)–C(4)–C(7)–C(6)–C(5) and the resulting conformation is intermediate between envelope ^2E and and twist ^2_1T forms. The values of the pseudorotational parameters τ_m and P correspond to one of the zones of high population density in the conformational wheel defined in a recent statistical study performed over a large number of sugar rings (Murray-Rust & Motherwell, 1978).

Molecular conformation. The orientation of imidazoline with respect to furanose is *anti*. The glycosidic torsion angle O(1)–C(4)–C(3)–C(2) (Sundaralingam, 1969) is 24·6 (7)°. In a previous structural analysis of imidazole *C*-nucleosides both *syn* and *anti* conformations were found but more data are necessary in order to correlate the glycosidic torsion angle with the sugar conformation.

Table 3 shows the torsion angles describing the conformation of the groups.

Crystal packing. Fig. 2 shows the contents of the unit cell viewed along **c**. Packing is due to hydrogen bonds linking the molecules through the water molecules.

The structure consists of helical chains parallel to **b**. In these chains each molecule is linked by hydrogen bonds to the nearest neighbors related by a twofold screw axis. These chains are also linked by hydrogen bonds to give a two-dimensional pattern parallel to (100). Details of these contacts are given in Table 4. No other intermolecular contacts shorter than the sum of the van der Waals radii have been detected.

The authors thank Professor Fernández-Bolaños for supplying the crystals and the staff of the 'Instituto Rocasolano' of CSIC (Madrid) for collecting the data. The present work forms part of a program supported by the Government through the 'Comisión Asesora de Investigación Científica y Técnica'.

Table 2. *Least-squares planes through molecular groups*

(*a*) Equations of the planes (X, Y and Z are orthogonal Cartesian coordinates)

(I) Imidazoline ring
$-0{\cdot}56452X - 0{\cdot}24764Y - 0{\cdot}78739Z + 6{\cdot}06402 = 0$

(II) Furanose ring
$0{\cdot}35519X - 0{\cdot}18143Y - 0{\cdot}91702Z + 3{\cdot}28805 = 0$

(*III*) Phenyl ring
$-0{\cdot}08839X - 0{\cdot}74040Y - 0{\cdot}66633Z + 6{\cdot}77294 = 0$

(*b*) Atomic deviations (Å)

(I)		(II)		(III)	
C(2)	−0·004 (6)	C(6)	−0·182 (6)	C(8)	−0·005 (5)
N(2)	−0·001 (5)	C(7)	0·250 (6)	C(9)	0·004 (6)
C(1)	0·005 (6)	C(4)	−0·233 (6)	C(10)	0·005 (6)
N(1)	−0·005 (5)	O(1)	0·082 (5)	C(11)	−0·010 (6)
C(3)	0·009 (6)	C(5)	0·051 (8)	C(12)	0·008 (6)
		O(3)*	−0·244 (4)	C(13)	0·001 (6)
		O(2)*	−1·549 (4)		
		C(3)*	0·495 (6)		

* Atoms not included in the least-squares calculations.

Table 3. *Selected torsion angles* (°)

C(1)–N(1)–C(8)–C(9)	−44·4 (7)	O(1)–C(4)–C(7)–C(6)	40·5 (5)
C(2)–N(1)–C(8)–C(13)	−35·6 (7)	C(4)–C(7)–C(6)–C(5)	−36·4 (5)
C(7)–C(4)–C(3)–N(2)	88·3 (6)	C(7)–C(6)–C(5)–O(1)	20·5 (6)
O(1)–C(4)–C(3)–C(2)	24·6 (7)	C(6)–C(5)–O(1)–C(4)	5·1 (6)
C(5)–O(1)–C(4)–C(7)	−28·6 (5)		

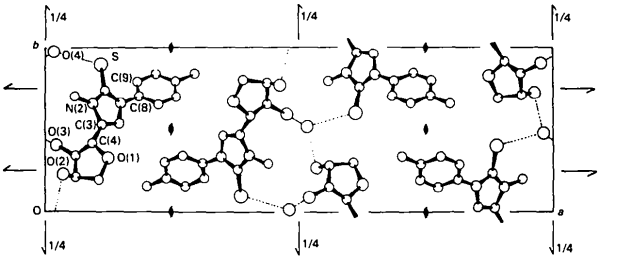

Fig. 2. A view of the unit-cell contents along **c**.

Table 4. *Intermolecular hydrogen bonds* (*distances in* Å, *angles in* deg)

X–H···*Y*	*X*···*Y*	*X*–H	H···*Y*	*X*–H···*Y*	H–*X*···*Y*
O(2)–H(O2)···O(4^{i})	2·792 (5)	0·93 (7)	1·96 (7)	159 (6)	15 (4)
O(3)–H(O3)···O(4^{ii})	2·869 (5)	0·94 (6)	1·94 (6)	167 (6)	9 (4)
O(4)–H(104)···O(3^{iii})	2·799 (5)	0·88 (7)	1·93 (7)	171 (6)	6 (4)
O(4)–H(204)···S^{iv}	3·231 (4)	0·96 (6)	2·27 (6)	178 (5)	2 (4)

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

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Structure of 6,7-Dimethyl-4aβ,5,8,8aβ-tetrahydronaphthoquin-1α,4α-diol,* $C_{12}H_{18}O_2$

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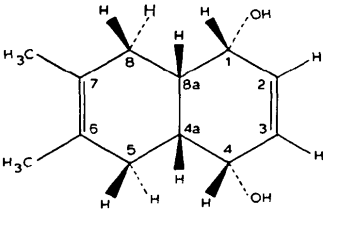
Abstract. $M_r = 194{\cdot}28$, monoclinic, $P2_1/c$, $a = 13{\cdot}870$ (2), $b = 18{\cdot}025$ (4), $c = 9{\cdot}236$ (1) Å, $\beta = 108{\cdot}098$ (6)°, $V = 2194{\cdot}9$ (6) Å^3, $Z = 8$, $D_x = 1{\cdot}176$, D_o (flotation) $= 1{\cdot}179$ g cm^{-3}, $T = 295$ K, $F(000) = 848$, μ(Mo $K\alpha$) $= 0{\cdot}436$ cm^{-1}, $\lambda = 0{\cdot}71073$ Å, $R = 0{\cdot}032$ for 1461 observed data. Extensive hydrogen bonding links molecules in a three-dimensional network, with disorder of one of the hydroxyl H atoms. A structural comparison of the present compound with conformationally similar tetrahydronaphthoquinols is presented.

Introduction. Obtaining single crystals for X-ray diffraction work has in many cases been the determining factor in whether or not the solid-state structure is solved. This limitation has led to a project of investigating solid-state structures by ^{13}C NMR spectroscopy. McDowell, Naito, Scheffer & Wong (1981) have illustrated some advantages of this technique over X-ray structure analysis in their work on conformational analysis of tetrahydronaphthoquinones.

McDowell *et al.* have shown that for the tetrahydronaphthoquinones, where chemically equivalent C atoms appear as singlets in solution, doublets appear in the solid state. This is attributed to the slight environmental differences experienced by the C atoms in the solid state. It was proposed that this discriminating feature of the solid state could be exploited in identifying structurally independent molecules whose ^{13}C NMR spectra should be readily discernible.

Although the characterization of the two structurally independent molecules of unsubstituted 4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone in the solid state was successful, such was not the case for the present compound (I). The multitude of peaks in the ^{13}C NMR spectrum suggested more than one independent molecule in the structure but the evidence did not unambiguously indicate the exact number.



(I)

This crystallographic analysis was undertaken in an effort (i) to establish the number of structurally independent molecules, (ii) to establish their individual conformations and if they differed from each other and (iii) to verify the isomer (with respect to the OH positions) present. Of additional interest crystallographically was how the present, fully reduced structure compared with derivatives of 4aβ,5,8,8aβ-tetrahydro-1-naphthoquin-4α-ol.

* IUPAC name: 6,7-dimethyl-1,4,4aβ,5,8,8aβ-hexahydronaphthalene-1α,4α-diol.

0108-2701/83/010125-04$01.50