The two symmetry-related molecules form a dimer linked by two equivalent O(1)—H(O)···O(2') hydrogen bonds, with characteristic values: H(O)···O(2') 2·00 (3) Å, O(1)···O(2') 2·806 (2) Å, O(1)—H(O)—O(2') 165 (1)°. No other short intermolecular contact distances occur in the structure.

References

BELLINGER, O. (1983). *Stereoselektive Synthesen von exo- und endo-Tricyclo[4.2.1.0²·⁵]nonanonderivaten*. Thesis, Univ. of Frankfurt/Main.

CHENG, P.-T. & NYBURG, S. C. (1976). *Acta Cryst.* B32, 930–932.

CHENG, P.-T., WONG-NG, W. K., NYBURG, S. C. & VAN DER HEIJDEN, S. (1976). *Acta Cryst.* B32, 933–935.

DESTRO, R., FILIPPINI, G., GRAMACCIOLI, C. M. & SIMONETTA, M. (1969). *Acta Cryst.* B25, 2465–2472.

ENRAF–NONIUS (1981). *Structure Determination Package*. Enraf–Nonius, Delft.

FILIPPINI, G., GRAMACCIOLI, C. M., ROVERE, C. & SIMONETTA, M. (1972). *Acta Cryst.* B28, 2869–2874.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Structure of 5,2'-Anhydro-5-(p-toluenesulfonamido)-1-(3'-O-tosyl-β-D-arabinofuranosyl)imidazole-4-carbonitrile, C₂₃H₂₂N₄O₇S₂

BY SHIGETOSHI SUGIO, HIROSHI MIZUNO, KUNIHIRO KITAMURA, MORIO IKEHARA AND KEN-ICHI TOMITA

Faculty of Pharmaceutical Sciences, Osaka University, 1-6 Yamada-oka, Suita, Osaka 565, Japan

Abstract. $M_r = 530.57$, monoclinic, $P2_1$, $a = 11.099$ (1), $b = 11.015$ (1), $c = 10.114$ (1) Å, $\beta = 92.27$ (2)°, $V = 1235.6$ (3) Å³, $Z = 2$, $D_m = 1.404$ (1), $D_x = 1.426$ Mg m⁻³, Zr-filtered Mo $K\alpha$, $\lambda = 0.70924$ Å, $\mu = 0.267$ mm⁻¹, $F(000) = 552$, $T = 293$ K, final $R = 0.033$ for 2764 reflections. The glycosyl torsion angle $\chi[C(2)—N(1)—C(1')—O(4')]$ is -74.2 (2)° and the furanose ring is in the C(4')-endo–C(3')-exo (⁴T₃) conformation.

Introduction. The present study is one of a series of crystal structure analyses of nucleosides containing the imidazole ring. The title compound is the first nucleoside to be solved as a cyclic nucleoside formed between imidazole and the furanose ring through the N atom. The effect of stereochemical restriction by such a cyclization was investigated by comparison with the previously solved structure of 1-(5'-O-acetyl-2',3'-O-isopropylidene-β-D-ribofuranosyl)-5-ditosylaminoimidazole-4-carbonitrile (Kitamura, Mizuno, Sugio, Okabe, Ikehara & Tomita, 1983).

Experimental. Colorless prismatic crystals from water–ethanol solution at room temperature; density by flotation. Cell dimensions by least-squares refinement of 2θ values of 19 reflections with $18° \le 2\theta \le 34°$. Crystal $0.2 \times 0.2 \times 0.3$ mm. Rigaku–Denki AFC-4 automated diffractometer, Zr-filtered Mo $K\alpha$ radiation, $2\theta_{max} = 55°$, θ–2θ scan technique. 3000 independent reflections, $0 \le h \le 14$, $0 \le k \le 14$ and $-13 \le l \le 13$, 2764 with $|F_o| > 3\sigma(F_o)$. Three standard reflections (500, 040 and 004) monitored after every 61 reflections; <0.9 (6)% intensity fluctuation. Intensities corrected for Lorentz and polarization factors but not for absorption. Direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Positional and anisotropic thermal parameters for all non-H atoms refined by block-diagonal least squares (*HBLSV*; Ashida, 1979); $w(|F_o| - k|F_c|)^2$ minimized; $w = [\sigma^2(F_o) + 0.0042|F_o| + 0.0001|F_o|^2]^{-1}$. All H atoms located on a difference Fourier map; their positional parameters included in the refinement with a fixed isotropic thermal parameter of 3·0 Å². Final R and R_w for 2764 reflections 0·033 and 0·043; S for 414 parameters (nine for each non-H atom, four for each H atom and two for overall scale and thermal parameters) = 1·385. In final cycle $(\Delta/\sigma)_{mean}$ and $(\Delta/\sigma)_{max}$, 0·020 and 0·083, respectively for non-H atoms. Maximum and minimum heights on final difference Fourier map 0·17 and -0.16 e Å⁻³; no other significant features observed. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). ACOS 900 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Discussion. The final atomic coordinates for non-H atoms with their estimated standard deviations are

given in Table 1* and bond distances and angles in Table 2. A drawing of the molecule and the numbering for the individual atoms are shown in Fig. 1.

The fused five-membered ring is essentially coplanar with the imidazole ring. The formation of the N(5)—C(2') bond influences changes in the bond angles: the major changes are in C(2)—N(1)—C(1') and in C(4)—C(5)—N(5) which are about 12–13° larger respectively than those in non-cyclo imidazole nucleosides (Kitamura, Mizuno, Sugio, Okabe, Ikehara & Tomita, 1983). The latter angle is also larger than the corresponding angle N(7)—C(8)—O(2') in 8,2'-O-cyclo-adenosine (129·7°) (Neidle, Taylor & Cowling, 1979) and N(7)—C(8)—S in 8,2'-S-cyclo-5'-AMP (131·1°) (Tanaka, Fujii, Fujiwara & Tomita, 1979). It is interesting to note that a weak intramolecular electrostatic interaction exists between C(6) and O(12) [C(6)—O(12) = 2·862 (4) Å]. Of the angles around the S atoms, O(3')—S(2)—C(21) (96·9°) is considerably smaller, but O(11)—S(1)—O(12) (121·6°) is larger than the tetrahedral angle.

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38887 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters and equivalent isotropic thermal parameters for the non-*H *atoms, with estimated standard deviations in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	B_{eq}(Å²)
N(1)	0·4706 (2)	0·1897 (2)	0·1876 (2)	3·26 (1)
C(2)	0·4779 (2)	0·1166 (2)	0·0803 (3)	4·02 (2)
N(3)	0·5596 (2)	0·1572 (2)	0·0011 (2)	4·18 (2)
C(4)	0·6062 (2)	0·2622 (2)	0·0592 (2)	3·47 (2)
C(5)	0·5520 (2)	0·2797 (2)	0·1767 (2)	3·03 (2)
N(5)	0·5468 (2)	0·3566 (2)	0·2851 (2)	3·27 (2)
C(6)	0·6902 (2)	0·3340 (3)	−0·0093 (3)	4·25 (2)
N(6)	0·7537 (2)	0·3912 (3)	−0·0684 (3)	5·94 (3)
S(1)	0·6612 (1)	0·4449	0·3349 (1)	3·36 (1)
O(11)	0·6130 (2)	0·5221 (2)	0·4322 (2)	4·64 (2)
O(12)	0·7050 (2)	0·4917 (2)	0·2156 (2)	4·64 (2)
C(11)	0·7701 (2)	0·3505 (2)	0·4092 (2)	3·38 (2)
C(12)	0·8615 (2)	0·3072 (3)	0·3330 (2)	4·01 (2)
C(13)	0·9482 (2)	0·2327 (3)	0·3903 (3)	4·85 (3)
C(14)	0·9439 (3)	0·1995 (3)	0·5226 (3)	5·32 (3)
C(15)	0·8516 (3)	0·2444 (3)	0·5967 (3)	5·32 (3)
C(16)	0·7647 (2)	0·3205 (3)	0·5413 (3)	4·52 (3)
C(17)	1·0366 (4)	0·1185 (5)	0·5829 (5)	8·45 (5)
C(1')	0·3981 (2)	0·1995 (2)	0·3038 (2)	3·25 (2)
C(2')	0·4621 (2)	0·3050 (2)	0·3795 (2)	3·09 (2)
C(3')	0·3609 (2)	0·3956 (2)	0·4037 (2)	3·14 (2)
O(3')	0·3075 (1)	0·3654 (2)	0·5281 (1)	3·60 (1)
C(4')	0·2670 (2)	0·3667 (2)	0·2957 (2)	3·35 (2)
O(4')	0·2789 (1)	0·2380 (2)	0·2728 (2)	3·57 (1)
C(5')	0·2826 (2)	0·4384 (3)	0·1677 (2)	4·03 (2)
O(5')	0·2822 (2)	0·5618 (2)	0·1950 (2)	6·42 (3)
S(2)	0·3553 (1)	0·4377 (1)	0·6560 (1)	3·38 (1)
O(21)	0·3323 (2)	0·5632 (2)	0·6352 (2)	4·87 (2)
O(22)	0·4757 (2)	0·4007 (2)	0·6882 (2)	4·86 (2)
C(21)	0·2560 (2)	0·3743 (2)	0·7662 (2)	3·32 (2)
C(22)	0·1416 (2)	0·4241 (3)	0·7758 (3)	4·26 (2)
C(23)	0·0607 (2)	0·3673 (3)	0·8559 (3)	4·70 (3)
C(24)	0·0911 (2)	0·2626 (3)	0·9243 (3)	4·21 (2)
C(25)	0·2078 (3)	0·2165 (3)	0·9145 (2)	4·20 (2)
C(26)	0·2896 (2)	0·2714 (2)	0·8352 (2)	3·82 (2)
C(27)	0·0027 (4)	0·1945 (5)	1·0059 (4)	6·80 (4)

Table 2. *Bond distances* (Å) *and angles* (°) *for non*-H *atoms*

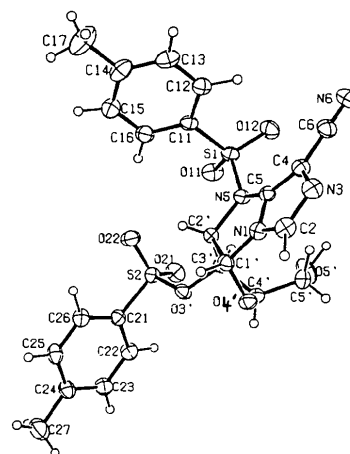| N(1)—C(2)	1·356 (3)	N(1)—C(5)	1·349 (3)
N(1)—C(1')	1·454 (3)	C(2)—N(3)	1·312 (4)
N(3)—C(4)	1·388 (3)	C(4)—C(5)	1·367 (3)
C(4)—C(6)	1·423 (4)	C(5)—N(5)	1·388 (3)
N(5)—S(1)	1·662 (2)	N(5)—C(2')	1·480 (3)
C(6)—N(6)	1·133 (4)	S(1)—O(11)	1·421 (2)
S(1)—O(12)	1·416 (2)	S(1)—C(11)	1·742 (3)
C(11)—C(12)	1·383 (4)	C(11)—C(16)	1·380 (4)
C(12)—C(13)	1·375 (4)	C(13)—C(14)	1·390 (5)
C(14)—C(15)	1·384 (5)	C(14)—C(17)	1·475 (6)
C(15)—C(16)	1·380 (5)	C(1')—O(4')	1·413 (3)
C(1')—C(2')	1·549 (4)	O(4')—C(4')	1·443 (3)
C(2')—C(3')	1·529 (4)	C(3')—O(3')	1·451 (3)
C(3')—C(4')	1·513 (3)	O(3')—S(2)	1·592 (2)
C(4')—C(5')	1·532 (4)	C(5')—O(5')	1·387 (4)
S(2)—O(21)	1·420 (2)	S(2)—O(22)	1·422 (3)
S(2)—C(21)	1·744 (3)	C(21)—C(22)	1·390 (4)
C(21)—C(26)	1·375 (4)	C(22)—C(23)	1·383 (4)
C(23)—C(24)	1·380 (4)	C(24)—C(25)	1·398 (4)
C(24)—C(27)	1·507 (6)	C(25)—C(26)	1·375 (4)
C(2)—N(1)—C(5)	108·0 (2)	N(1)—C(1')—O(4')	112·7 (2)
C(2)—N(1)—C(1')	138·0 (2)	N(1)—C(1')—C(2')	101·4 (2)
C(5)—N(1)—C(1')	113·9 (2)	O(4')—C(1')—C(2')	107·0 (2)
N(1)—C(2)—N(3)	110·5 (2)	C(1')—O(4')—C(4')	110·5 (2)
C(2)—N(3)—C(4)	106·3 (2)	N(5)—C(2')—C(1')	105·1 (2)
N(3)—C(4)—C(5)	108·4 (2)	N(5)—C(2')—C(3')	110·0 (2)
N(3)—C(4)—C(6)	119·8 (2)	C(1')—C(2')—C(3')	104·1 (2)
C(5)—C(4)—C(6)	131·6 (2)	C(2')—C(3')—O(3')	108·5 (2)
N(1)—C(5)—C(4)	106·7 (2)	C(2')—C(3')—C(4')	103·7 (2)
N(1)—C(5)—N(5)	109·6 (2)	O(3')—C(3')—C(4')	106·5 (2)
C(4)—C(5)—N(5)	143·7 (2)	C(3')—O(3')—S(2)	117·1 (2)
C(5)—N(5)—S(1)	122·8 (2)	O(4')—C(4')—C(3')	104·9 (2)
C(5)—N(5)—C(2')	108·8 (2)	O(4')—C(4')—C(5')	110·9 (2)
S(1)—N(5)—C(2')	121·8 (2)	C(3')—C(4')—C(5')	113·8 (2)
C(4)—C(6)—N(6)	177·1 (3)	C(4')—C(5') O(5')	109·6 (2)
N(5)—S(1)—O(11)	104·8 (1)	O(3')—S(2)—O(21)	108·3 (1)
N(5)—S(1)—O(12)	103·8 (1)	O(3')—S(2)—O(22)	108·8 (1)
N(5)—S(1)—C(11)	106·9 (1)	O(3')—S(2)—C(21)	96·9 (1)
O(11)—S(1)—O(12)	121·6 (1)	O(21)—S(2)—O(22)	118·3 (1)
O(11)—S(1)—C(11)	109·4 (1)	O(21)—S(2)—C(21)	111·7 (1)
O(12)—S(1)—C(11)	109·2 (1)	O(22)—S(2)—C(21)	110·5 (1)
S(1)—C(11)—C(12)	118·5 (2)	S(2)—C(21)—C(22)	119·3 (2)
S(1)—C(11)—C(16)	120·3 (2)	S(2)—C(21)—C(26)	119·3 (2)
C(12)—C(11)—C(16)	121·2 (3)	C(22)—C(21)—C(26)	121·3 (2)
C(11)—C(12)—C(13)	119·2 (3)	C(21)—C(22)—C(23)	118·6 (3)
C(12)—C(13)—C(14)	120·8 (3)	C(22)—C(23)—C(24)	121·4 (3)
C(13)—C(14)—C(15)	118·8 (3)	C(23)—C(24)—C(25)	118·5 (3)
C(13)—C(14)—C(17)	120·5 (4)	C(23)—C(24)—C(27)	122·6 (3)
C(15)—C(14)—C(17)	120·7 (4)	C(25)—C(24)—C(27)	118·9 (3)
C(14) C(15)—C(16)	121·2 (3)	C(24)—C(25)—C(26)	121·1 (3)
C(11)—C(16)—C(15)	118·8 (3)	C(21)—C(26)—C(25)	119·1 (2)

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the molecule and the numbering for the individual atoms. Non-H atoms are represented by 30% probability thermal ellipsoids.
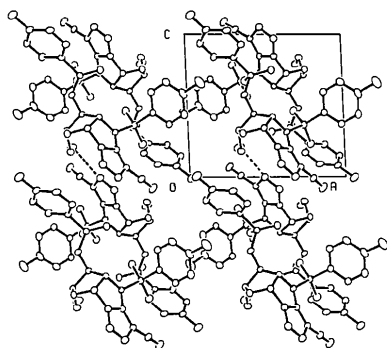
$C_{23}H_{22}N_4O_7S_2$

Fig. 2. Molecular packing viewed down the b axis.

The glycosyl torsion angle C(2)—N(1)—C(1')—O(4') is −74·2 (2)°. The sugar pucker is in a twisted form, C(4')-endo–C(3')-exo, with pseudorotation angle P = 220·9° as defined by Altona & Sundaralingam (1972). A similar conformation is also observed in 8,2'-O-cycloadenosine (P = 217·5°) and in 8,2'-S-cyclo-5'-AMP (P = 232·7°).

The molecular packing is illustrated in Fig. 2. A hydrogen bond is observed between O(5') and N(3) in the neighbouring molecule related by the 2_1 screw axis.

References

ALTONA, C. & SUNDARALINGAM, M. (1972). J. Am. Chem. Soc. 94, 8205–8212.
ASHIDA, T. (1979). HBLSV. The Universal Crystallographic Computing System–Osaka. Library of Programs, Computing Center, Osaka Univ.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
KITAMURA, K., MIZUNO, H., SUGIO, S., OKABE, N., IKEHARA, M. & TOMITA, K. (1983). Acta Cryst. C39, 1551–1553.
MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.
NEIDLE, S., TAYLOR, G. L. & COWLING, P. C. (1979). Acta Cryst. B35, 708–712.
TANAKA, K., FUJII, S., FUJIWARA, T. & TOMITA, K. (1979). Acta Cryst. B35, 929–933.

Structure of 1-(p-Ethoxyphenyl)-1,3-dihydro-3-phenyl-2H-benzimidazole-2-thione, C21H18N2OS
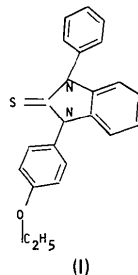
BY A. CRIADO, A. CONDE AND R. MÁRQUEZ

Departamento de Optica y Sección de Física del Centro Coordinado de CSIC, Universidad de Sevilla, Spain

Abstract. M_r = 346·4, orthorhombic, $P2_12_12_1$, a = 7·600 (1), b = 11·132 (2), c = 20·767 (3) Å, V = 1756·9 (5) Å^3, Z = 4, D_x = 1·31 Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ = 1·67 mm^{-1}, $F(000)$ = 728, T = 300 K. Final R = 0·049 for 1531 observed independent reflections. The benzimidázole bicycle is quasi-planar, the dihedral angle between the two fused rings being 1·6 (2)°. The unsubstituted phenyl ring is planar while the phenyl ring with the ethoxy substituent deviates significantly from the expected planar conformation.

Introduction. The crystal structure of the title compound has been determined as part of a systematic structural analysis of imidazole C-nucleosides synthesized in the Organic Chemistry Department of this University. Recently, we have reported (Criado, Conde & Márquez, 1983) the structure of the first disubstituted (at both N atoms) imidazole C-nucleoside.

The title compound (I) has been obtained (Fernández-Bolaños, Fuentes-Mota & Fernández-Bolaños Guzmán, 1983a) from the p-toluene-sulfonate of 4-(β-D-erythrofuranosyl)-1-(p-ethoxyphen-yl)-1,3-dihydro-3-phenyl-2H-imidazole-2-thione (Fernández-Bolaños, Fuentes-Mota & Fernández-Bolaños Guzmán, 1983b) using a reaction similar to that of Tipson & Cohen (1965). This synthesis is the first case of nucleoside aromatization.

(I)