Structure of 5,5'-Anhydro-5-benzenesulfonamido-1-(2',3'-*O*-isopropylidene-β-D-ribofuranosyl)imidazole-4-carbonitrile, C₁₈H₁₈N₄O₅S

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Abstract. $M_r = 402.42$, orthorhombic, $P2_12_12_1$, $a = 8.453$ (5), $b = 20.905$ (8), $c = 10.570$ (3) Å, $V = 1868$ (1) Å³, $Z = 4$, $D_m = 1.432$ (2), $D_x = 1.431$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 1.85$ mm⁻¹, $F(000) = 840$, $T = 293$ K, final $R = 0.055$ for 1316 observed reflections. The glycosyl torsion angle is $-107.2°$, and the furanose-ring conformation is C(4')-endo–O(4')-exo (^4T_O). The cyano fragment is significantly non-linear [C(4)–C(6)–N(6) 175.9°] and C(6)–N(6) stacks parallel to the benzene ring. The crystal structure is stabilized solely by van der Waals contacts.

Introduction. The present analysis is one of a series of crystal structure studies of nucleosides containing the imidazole ring. The title compound is a cyclic nucleoside linked between the imidazole and furanose rings through C(5') instead of C(2') which was previously reported (Sugio, Kitamura, Mizuno, Ikehara & Tomita, 1984). The conformation influenced by such a cyclization has been studied and compared with those found in related nucleosides.

Experimental. Colorless prismatic crystals from water–ethanol at room temperature. Crystal 0.2 × 0.2 × 0.15 mm. D_m by flotation. Cell dimensions by least-squares refinement of 18 reflections with $2\theta = 34$–72°. Rigaku AFC-3 automated diffractometer, Ni-filtered Cu $K\alpha$ radiation, $2\theta_{max} = 120°$, θ–2θ scan technique. Of 1640 independent reflections ($0 \le h \le 9, 0 \le k \le 23, 0 \le l \le 11$), 1320 had $|F_o| > 3\sigma(F_o)$. Three standard reflections (200, 040, 002) monitored after every 50 reflections showed 1.4 (6)% intensity fluctuation throughout data collection. 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). $\sum w(|F_o| - k|F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0.0490|F_o| + 0.0009|F_o|^2]^{-1}$. All H atoms located on a difference Fourier map; their positional parameters included in refinement with a fixed isotropic thermal parameter of 4.0 Å². Four intense low-angle reflections (020, 012, 140, 150) affected by secondary extinction and excluded. Final R and wR for 1316 reflections 0.055 and 0.067, respectively. S for 326 parameters (nine for each non-H atom, four for each H atom, an overall scale and an overall thermal parameter) is 1.058. $(\Delta/\sigma)_{av} = 0.051$, $(\Delta/\sigma)_{max} = 0.453$ for non-H atoms. $\Delta\rho = -0.19$ to 0.22 e Å⁻³, no other significant features observed. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations performed on an ACOS 900 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Discussion. Final atomic coordinates for non-H atoms with their e.s.d.'s are given in Table 1, and bond distances and angles in Table 2.* A perspective view of the molecule is shown in Fig. 1. Although the hybrid orbital of N(5) is sp^2, dihedral angles [N(1)–C(5)–N(5)–S(1) = 105.3 (6) and N(1)–C(5)–N(5)–C(5') = −64.5 (8)°] suggest that the N(5) lone-pair axis is nearly perpendicular to the normal of the imidazole plane as was seen in a bulky substituted non-cyclic imidazole nucleoside (Kitamura, Mizuno, Sugio, Okabe, Ikehara & Tomita, 1983).

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39494 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
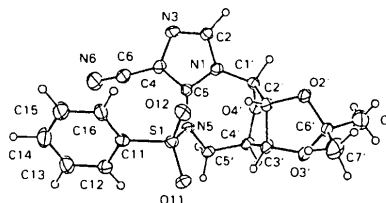

Fig. 1. Perspective drawing of the molecule (Johnson, 1976). Thermal ellipsoids correspond to 30% probability surfaces.

Table 1. *Final positional and equivalent isotropic thermal parameters for the non-H atoms with e.s.d.'s in parentheses*

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

	x	y	z	$B_{eq}(\text{Å}^2)$
N(1)	0·9806 (6)	−0·0583 (2)	0·7578 (5)	2·93 (4)
C(2)	1·0759 (8)	−0·0648 (3)	0·8620 (6)	3·41 (6)
N(3)	1·1822 (7)	−0·0203 (3)	0·8680 (5)	3·99 (5)
C(4)	1·1606 (8)	0·0158 (3)	0·7595 (6)	3·30 (6)
C(5)	1·0326 (7)	−0·0065 (3)	0·6914 (6)	2·85 (5)
N(5)	0·9602 (6)	0·0116 (2)	0·5792 (5)	2·79 (4)
C(6)	1·2666 (9)	0·0658 (4)	0·7255 (8)	4·57 (7)
N(6)	1·3575 (9)	0·1044 (4)	0·7035 (8)	7·05 (9)
S(1)	0·8449 (2)	0·0755 (1)	0·5846 (2)	2·87 (1)
O(11)	0·7615 (6)	0·0762 (2)	0·4667 (4)	4·22 (5)
O(12)	0·7606 (6)	0·0737 (2)	0·7018 (4)	4·02 (4)
C(11)	0·9742 (7)	0·1417 (3)	0·5900 (6)	2·97 (5)
C(12)	1·0638 (9)	0·1559 (3)	0·4834 (7)	3·79 (6)
C(13)	1·165 (1)	0·2078 (3)	0·4904 (8)	4·94 (8)
C(14)	1·176 (1)	0·2434 (4)	0·5987 (8)	5·43 (9)
C(15)	1·087 (1)	0·2282 (4)	0·7028 (8)	5·9 (1)
C(16)	0·984 (1)	0·1773 (3)	0·6988 (7)	4·34 (8)
C(1′)	0·8747 (8)	−0·1077 (3)	0·7074 (6)	3·07 (5)
C(2′)	0·7081 (7)	−0·0854 (3)	0·6721 (6)	3·02 (6)
O(2′)	0·6007 (6)	−0·1347 (2)	0·7064 (4)	4·43 (5)
C(3′)	0·7047 (8)	−0·0847 (3)	0·5258 (6)	3·33 (6)
O(3′)	0·6201 (6)	−0·1416 (2)	0·4942 (4)	4·16 (5)
C(4′)	0·8787 (8)	−0·0948 (3)	0·4901 (6)	3·17 (6)
O(4′)	0·9412 (5)	−0·1322 (2)	0·5930 (4)	3·35 (4)
C(5′)	0·9679 (8)	−0·0325 (3)	0·4693 (6)	3·02 (6)
C(6′)	0·5187 (8)	−0·1571 (3)	0·5958 (7)	3·62 (6)
C(7′)	0·3632 (9)	−0·1202 (4)	0·583 (1)	6·2 (1)
C(8′)	0·4977 (2)	−0·2274 (4)	0·6042 (9)	6·21 (9)

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

N(1)—C(2)	1·371 (9)	N(1)—C(5)	1·363 (8)
N(1)—C(1′)	1·467 (9)	C(2)—N(3)	1·295 (9)
N(3)—C(4)	1·385 (9)	C(4)—C(5)	1·381 (9)
C(4)—C(6)	1·42 (1)	C(5)—N(5)	1·387 (8)
N(5)—S(1)	1·655 (5)	N(5)—C(5′)	1·484 (8)
C(6)—N(6)	1·14 (1)	S(1)—O(11)	1·432 (5)
S(1)—O(12)	1·430 (5)	S(1)—C(11)	1·764 (7)
C(11)—C(12)	1·39 (1)	C(11)—C(16)	1·37 (1)
C(12)—C(13)	1·39 (1)	C(13)—C(14)	1·37 (1)
C(14)—C(15)	1·37 (1)	C(15)—C(16)	1·37 (1)
C(1′)—O(4′)	1·428 (8)	C(1′)—C(2′)	1·53 (1)
O(4′)—C(4′)	1·440 (8)	C(2′)—O(2′)	1·420 (8)
C(2′)—C(3′)	1·55 (1)	O(2′)—C(6′)	1·437 (9)
C(3′)—O(3′)	1·428 (9)	C(3′)—C(4′)	1·53 (1)
O(3′)—C(6′)	1·412 (8)	C(4′)—C(5′)	1·521 (9)
C(6′)—C(7′)	1·53 (1)	C(6′)—C(8′)	1·48 (1)

C(2)—N(1)—C(5)	107·6 (5)	C(13)—C(14)—C(15)	120·4 (9)
C(2)—N(1)—C(1′)	125·5 (5)	C(14)—C(15)—C(16)	120·2 (9)
C(5)—N(1)—C(1′)	124·7 (5)	C(11)—C(16)—C(15)	118·9 (8)
N(1)—C(2)—N(3)	112·1 (6)	N(1)—C(1′)—O(4′)	108·6 (5)
C(2)—N(3)—C(4)	105·0 (6)	N(1)—C(1′)—C(2′)	115·8 (5)
N(3)—C(4)—C(5)	110·6 (6)	O(4′)—C(1′)—C(2′)	105·4 (5)
N(3)—C(4)—C(6)	121·8 (6)	C(1′)—O(4′)—C(4′)	107·5 (5)
C(5)—C(4)—C(6)	127·6 (6)	C(1′)—C(2′)—O(2′)	107·8 (5)
N(1)—C(5)—C(4)	104·6 (6)	C(1′)—C(2′)—C(3′)	105·3 (5)
N(1)—C(5)—N(5)	121·0 (6)	O(2′)—C(2′)—C(3′)	104·5 (5)
C(4)—C(5)—N(5)	134·4 (6)	C(2′)—O(2′)—C(6′)	109·7 (5)
C(5)—N(5)—S(1)	116·8 (4)	C(2′)—C(3′)—O(3′)	103·6 (5)
C(5)—N(5)—C(5′)	118·7 (5)	C(2′)—C(3′)—C(4′)	103·1 (6)
S(1)—N(5)—C(5′)	123·7 (4)	O(3′)—C(3′)—C(4′)	108·0 (6)
C(4)—C(6)—N(6)	175·9 (9)	C(3′)—O(3′)—C(6′)	108·5 (5)
N(5)—S(1)—O(11)	105·6 (3)	O(4′)—C(4′)—C(3′)	103·9 (5)
N(5)—S(1)—O(12)	107·6 (3)	O(4′)—C(4′)—C(5′)	113·1 (5)
N(5)—S(1)—C(11)	105·6 (3)	C(3′)—C(4′)—C(5′)	113·2 (6)
O(11)—S(1)—O(12)	120·6 (3)	N(5)—C(5′)—C(4′)	113·4 (5)
O(11)—S(1)—C(11)	109·0 (3)	O(2′)—C(6′)—O(3′)	104·5 (5)
O(12)—S(1)—C(11)	107·5 (3)	O(2′)—C(6′)—C(7′)	108·6 (6)
S(1)—C(11)—C(12)	118·6 (5)	O(2′)—C(6′)—C(8′)	109·4 (6)
S(1)—C(11)—C(16)	119·3 (6)	O(3′)—C(6′)—C(7′)	109·9 (6)
C(12)—C(11)—C(16)	122·1 (7)	O(3′)—C(6′)—C(8′)	110·2 (6)
C(11)—C(12)—C(13)	117·5 (7)	C(7′)—C(6′)—C(8′)	113·7 (7)
C(12)—C(13)—C(14)	120·9 (8)		

The cyano fragment C(4)—C(6)—N(6) is significantly non-linear (175·9°); C(6)—N(6) stacks parallel to the benzene ring at a distance of 3·22 Å.
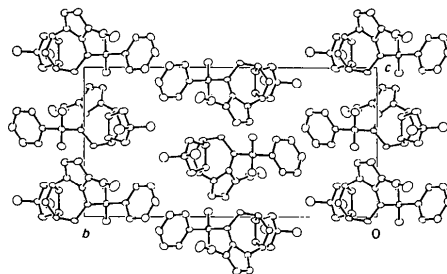
The seven-membered ring formed by cyclization takes the chair conformation as found for 8,5′-cyclonucleosides (Tomita, Nishida, Fujiwara & Ikehara, 1970; Asai, Anzai, Suzuki & Iwasaki, 1973; Sugio, Mizuno, Kitamura, Hamada, Ikehara & Tomita, 1983) with N(5) located over the center of the furanose ring.

The glycosyl torsion angle C(2)—N(1)—C(1′)—O(4′) is −107·2 (7)°. The furanose ring is in the twist conformation, C(4′)-*endo*-O(4′)-*exo* ($^4T_0$), with P = 244·0° and $\tau_m = 22\cdot8°$, defined by Altona & Sundaralingam (1972). This conformation is widely observed in cyclonucleosides which possess the seven-membered ring system (*e.g.* Sugio, Mizuno, Kitamura, Hamada, Ikehara & Tomita, 1983; Yamagata, Fukumoto, Fujii, Tomita, Maruyama & Honjo, 1983). Because of distortions caused by the attached isopropylidene group, the τ_m value is apparently smaller than that found in 8,5′-*O*-cyclo-A (42°) (Sugio, Mizuno, Kitamura, Hamada, Ikehara & Tomita, 1983) and in 6,5′-*O*-cyclo-C (44°) (Yamagata, Fukumoto, Fujii, Tomita, Maruyama & Honjo, 1983) which have no protecting group on the sugar moiety.

The crystal structure is stabilized solely by van der Waals contacts, having no hydrogen bonding or base stacking (see Fig. 2).

Fig. 2. Crystal structure viewed down the *a* axis (Johnson, 1976).

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Structure of N-[Bis(methylthio)methylene]cinnamamide, $C_{12}H_{13}NOS_2$

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Abstract. $M_r = 251 \cdot 34$, monoclinic, $P2_1/n$, $a = 14 \cdot 626$ (3), $b = 7 \cdot 144$ (1), $c = 11 \cdot 996$ (2) Å, $\beta = 90 \cdot 03$ (2)°, $V = 1253 \cdot 4$ (6) Å³, $Z = 4$, $D_m = 1 \cdot 326$ (3), $D_x = 1 \cdot 331$ (3) g cm⁻³, Mo $K\alpha$, $\lambda = 0 \cdot 7107$ Å, $\mu = 3 \cdot 51$ cm⁻¹, $F(000) = 528 \cdot 0$, $T = 293$ K, $R = 3 \cdot 5\%$ for 1455 significant reflections. Of particular interest is an intramolecular attractive interaction between the sulphur and oxygen atoms with an S···O distance of $2 \cdot 658$ (3) Å, in which the oxygen atom appears to act as a nucleophile.

Introduction. The existing programme in our laboratory to study the molecular geometry of push–pull ethylenes by X-ray structural analysis (Adhikesavalu, Kamath & Venkatesan, 1983) included a study of 3,3-bis(methylthio)-2-nitro-2-propene-1-nitrile (Kamath & Venkatesan, 1984) where we observed that even with a combination of weak donors [bis(methylthio) group] and weak acceptors (nitro and cyano groups) the C=C double-bond length [$1 \cdot 377$ (3) Å] indicated a small degree of polarization. Interested in the possible push–pull character of the C=N double bond we decided to study the title compound where the donor groups remain the same, but the acceptor groups are replaced by a cinnamoyl group. Another point of interest is the synthetic potential of this compound and those of other N-[bis(alkylthio)methylene]acylamides which react with a wide range of nucleophilic compounds and therefore present new possibilities in the synthesis of heterocycles (Augustin, Richter & Salas, 1980).

The X-ray crystallographic investigations revealed a noteworthy structural feature in the geometry of this molecule which has a bivalent S atom as part of a five-membered hetero ring closed by an intramolecular S···O interaction. The compound was kindly provided by Dr Monica Richter, Martin-Luther University, Halle-Wittenberg.

Experimental. Single crystals grown from methanol by slow evaporation. D_m by flotation in KI solution. Crystal approximately $0 \cdot 6 \times 0 \cdot 3 \times 0 \cdot 5$ mm. Preliminary Weissenberg photographs indicated crystal to be monoclinic. Nonius CAD-4 diffractometer; lattice parameters refined by least-squares fit to settings of 23 accurately centred reflections. Intensity data collected using monochromated Mo $K\alpha$ radiation, scan speed 1° min⁻¹, $\theta_{max} = 23°$. Three standard reflections (9$\bar{1}$0, 060, 5$\bar{2}$4) showed only statistical variation within ±2%. 1891 reflections collected, 1455 significant, $|F_o| \geq 3\sigma(|F_o|)$. No correction for absorption. h −15–16, k 0–7, l 0–13. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix refinement of scale factor, positional and anisotropic thermal parameters (isotropic for H, located from difference map), $R = 0 \cdot 035$, $R_w = 0 \cdot 041$, $S = 3 \cdot 42$; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 3 \cdot 981/\sigma^2(F)$. *SHELX*76 (Sheldrick, 1976) used for full-matrix refinement. Δ/σ for non-hydrogen atoms ~0·005; final difference Fourier synthesis featureless. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).*