C1*A*—C2*A*—C3*A*	110.0 (2)	C1*B*—C2*B*—C3*B*	110.4 (3)
C8*A*—C2*A*—O11*A*	109.0 (2)	C8*B*—C2*B*—O11*B*	109.3 (3)
C3*A*—C2*A*—O11*A*	105.5 (2)	C3*B*—C2*B*—O11*B*	105.1 (2)
C3*A*—C2*A*—C8*A*	110.6 (2)	C3*B*—C2*B*—C8*B*	111.1 (3)
C2*A*—C3*A*—C4*A*	112.9 (3)	C2*B*—C3*B*—C4*B*	113.1 (3)
C3*A*—C4*A*—C5*A*	112.1 (4)	C3*B*—C4*B*—C5*B*	111.5 (4)
C4*A*—C5*A*—C6*A*	110.1 (4)	C4*B*—C5*B*—C6*B*	110.5 (4)
C1*A*—C6*A*—C5*A*	111.9 (3)	C1*B*—C6*B*—C5*B*	113.2 (3)
C1*A*—C2′*A*—O12*A*	122.0 (3)	C1*B*—C2′*B*—O12*B*	121.9 (3)
C1*A*—C2′*A*—C3′*A*	118.3 (3)	C1*B*—C2′*B*—C3′*B*	118.4 (3)
C3′*A*—C2′*A*—O12*A*	119.6 (3)	C3′*B*—C2′*B*—O12*B*	119.6 (3)
C2′*A*—C3′*A*—C4′*A*	123.8 (3)	C2′*B*—C3′*B*—C4′*B*	124.6 (3)
C3′*A*—C4′*A*—C7*A*	121.8 (3)	C3′*B*—C4′*B*—C7*B*	122.8 (3)
C3′*A*—C4′*A*—C5′*A*	121.2 (3)	C3′*B*—C4′*B*—C5′*B*	120.6 (3)
C5′*A*—C4′*A*—C7*A*	117.0 (3)	C5′*B*—C4′*B*—C7*B*	116.6 (3)
C4′*A*—C5′*A*—C6′*A*	111.9 (3)	C4′*B*—C5′*B*—C6′*B*	112.4 (4)
C1*A*—C6′*A*—C5′*A*	113.2 (2)	C1*B*—C6′*B*—C5′*B*	113.8 (3)
C2*A*—C8*A*—C9*A*	113.6 (3)	C2*B*—C8*B*—C9*B*	115.3 (3)
C8*A*—C9*A*—C10*A*	178.6 (4)	C8*B*—C9*B*—C10*B*	178.1 (4)

Table 3. *Ring-puckering parameters according to Cremer & Pople (1975)*

	Q (Å)	θ (°)	φ (°)
Molecule *A*			
Ring 1	0.580 (3)	177.0 (3)	154 (6)
Ring 2	0.460 (3)	126.8 (4)	109.2 (5)
Molecule *B*			
Ring 1	0.573 (4)	2.6 (4)	350 (9)
Ring 2	0.449 (3)	52.8 (4)	311.5 (6)

Table 4. *Hydrogen-bond parameters (Å, °)*

D—H···O	*D*—H	H···O	*D*···O	H_{norm}···O	*D*—H_{norm}···O
O11*A*—H···O12*A*	0.78 (4)	1.93 (4)	2.668 (4)	1.75	154
O11*B*—H···O12*B*	0.91 (8)	2.03 (3)	2.659 (4)	1.99	124
C10*A*—H···O11*B*	0.89 (4)	2.54 (5)	3.413 (4)	2.37	162
C10*B*—H···O11*A*	0.92 (3)	2.50 (5)	3.414 (5)	2.36	164

The structure was solved by direct methods. The initial *R* index for the model was 0.19. After a few cycles of full-matrix refinement the *R* index dropped to 0.12. All H atoms were located from difference Fourier maps and refined isotropically. The Flack χ parameter refined to −0.16 (32).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The α-Pyridyl Nucleoside Analogue 2-Bromo-5-(2-deoxy-α-D-ribofuranosyl)-pyridine

STEPHEN NEIDLE,[a]* DANIEL C. CAPALDI,[b] JOSEPH V. BERNADETTE[b] AND COLIN B. REESE[b]

[a]*CRC Biomolecular Structure Unit, The Institute of Cancer Research, Cotswold Road, Sutton, Surrey SM2 5NG, England, and* [b]*Department of Chemistry, King's College, Strand, London WC2R 2LS, England. E-mail: steve@iris5.icr.ac.uk*

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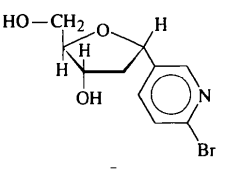
Abstract

The structure of the title compound, $C_{10}H_{12}BrNO_3$, is reported. The ribose sugar has a C3′-*endo* pucker and the exocyclic torsion angle O5′—C5′—C4′—C3′ adopts a *gauche*$^+$ value of 61.0 (9)°.

Comment

The determination of the structure of the title compound, (I), was undertaken in order to unequivocally assign the α-conformation at the C1′ atom following its synthesis as part of a project aimed at developing modified nucleosides for DNA triple-strand recognition. The details of the conformational features are being employed in molecular-modelling studies on triple helices with non-standard bases.



(I)

The structure and conformation of (I) show overall similarity to those of the non-brominated parent compound (II) (Ford, Neidle, Eaton, Millican & Mann, 1987). The C1′—C5 bond length [1.515 (7) Å] is close to that in (II) [1.510 (5) Å] and is significantly longer than the average glycosidic bond in standard nucleosides (1.46 Å). It is also slightly longer than the C1′—C bond in analogues of the α-anomer of the antibiotic showdomycin (Neidle, Kaye & Reese, 1990), which have an average bond length of 1.493 Å. These differences result in changes in the bond geometry of the furanose ring compared with that in standard nucleosides.

The conformational features of (I) are mostly similar to those found in (II) (Ford *et al.*, 1987). The furanose sugar ring in the title compound has a C3′-*endo* pucker with a pseudorotation parameter P of 5.9 (7)°, compared with a value of 324.5 (5)° and a C2′-*exo* pucker in (II). The orientation of the pyridine ring with respect to the sugar is very similar in the two structures, with values for the pseudo-glycosidic torsion angle O4′—C1′—C5—C6 of 135.0 (6)° in (I) and 126.2 (5)° in (II). The exocyclic torsion angle O5′—C5′—C4′—C3′ adopts a *gauche*$^+$ value of 61.0 (9)° in the title compound, whereas in the non-brominated compound it has a less common (Neidle, 1994) *trans* value of 177.2 (5)°. The *gauche*$^+$ value predominates in right-handed oligo- and polynucleotides.

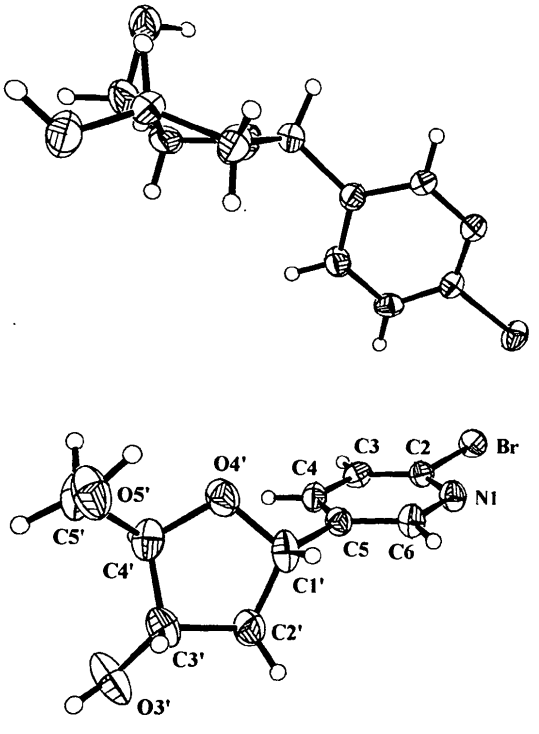


Fig. 1. Two orthogonal views of the title structure with displacement ellipsoids shown at the 50% probability level and H atoms drawn as small circles of arbitrary radii.

Experimental

Details of the synthesis of (I) will be published elsewhere.

Crystal data

$C_{10}H_{12}BrNO_3$
M_r = 274.1
Monoclinic
$P2_1$
a = 7.686 (3) Å
b = 7.2420 (10) Å
c = 9.9240 (10) Å
β = 98.31 (2)°
V = 546.6 (2) Å^3
Z = 2
D_x = 1.666 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 250 reflections
θ = 2–22°
μ = 3.747 mm^{-1}
T = 293 (2) K
Prism
0.5 × 0.2 × 0.1 mm
Colourless

Data collection

Enraf–Nonius FAST diffractometer
MADNESS (Enraf–Nonius, 1990) scans
Absorption correction: none
2486 measured reflections
1509 independent reflections
1426 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0686
θ_{max} = 24.75°
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -11 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0434
$wR(F^2)$ = 0.1139
S = 0.909
1509 reflections
136 parameters
H atoms treated using a riding model; U_{iso} values refined
$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.649 e Å^{-3}
$\Delta\rho_{min}$ = −0.518 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = −0.02 (2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Br	−0.17728 (6)	−0.32905 (10)	−0.65133 (5)	0.0494 (3)
N1	0.1762 (7)	−0.3998 (7)	−0.6064 (5)	0.0411 (12)
C2	0.0467 (7)	−0.3470 (11)	−0.5408 (5)	0.0358 (13)
C3	0.0616 (7)	−0.3069 (11)	−0.4052 (5)	0.0383 (14)
C4	0.2287 (8)	−0.3128 (13)	−0.3318 (5)	0.0410 (13)
C5	0.3702 (7)	−0.3607 (8)	−0.3948 (5)	0.0331 (14)
C6	0.3361 (7)	−0.4054 (8)	−0.5301 (6)	0.0373 (14)
C1′	0.5557 (8)	−0.3624 (10)	−0.3184 (6)	0.044 (2)
C2′	0.5944 (10)	−0.5220 (12)	−0.2204 (8)	0.050 (2)
C3′	0.7276 (8)	−0.4396 (11)	−0.1074 (7)	0.045 (2)
O3′	0.7344 (7)	−0.5361 (10)	0.0154 (5)	0.073 (2)
O4′	0.5822 (6)	−0.1994 (7)	−0.2377 (5)	0.0523 (14)
C4′	0.6576 (9)	−0.2457 (10)	−0.1029 (7)	0.043 (2)
C5′	0.7831 (10)	−0.0928 (12)	−0.0492 (7)	0.056 (2)
O5′	0.9213 (6)	−0.0741 (8)	−0.1308 (4)	0.0583 (13)

Data collection: *MADNESS* (Enraf–Nonius, 1990). Cell refinement: *MADNESS*. Data reduction: *MADNESS*. Program(s)

used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEX* (McArdle, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms, and torsion angles have been deposited with the IUCr (Reference: AS1213). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Phenylquinoline-4-carboxylic Acid

ANTHONY C. BLACKBURN, ALLISON J. DOBSON AND ROGER E. GERKIN

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: rgerkin@magnus.acs.ohio-state.edu

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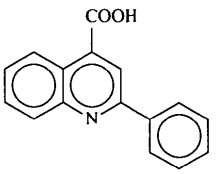
Abstract

In 2-phenylquinoline-4-carboxylic acid, $C_{16}H_{11}NO_2$, hydrogen bonding occurs only between a carboxy O-atom donor and the ring N atom, which acts as an acceptor. The carboxy H atom is ordered in this structure. The dihedral angle between the plane of the carboxy group and the best-fit mean quinoline plane is 53.6 (1)°. All bond distances and angles within the quinoline core, the carboxy group and the phenyl group fall within the normal ranges. The structure is described in space group $P2_12_12_1$

Comment

As part of a continuing series of investigations of hydrogen bonding in organic solids, we describe here the structure of 2-phenylquinoline-4-carboxylic acid, (I), the structure of which has not been reported previously.



(I)

The title molecule is shown in Fig. 1 with the numbering system and a stereoview of the structure is presented in Fig. 2. Selected bond lengths and angles are compiled in Table 2 and these data support the assignment of hydrogen bonds for this structure in which atom O(1) is the sole donor and the N atom of the quinoline moiety is the sole acceptor. Consistent with this, the carboxy H-atom position is ordered in this structure.

Takusagawa, Hirotsu & Shimada (1973) presented graphically a smooth curvilinear correlation between the N—$H_{carboxy}$ distance and the C—N—C_{ring} bond angle based upon their data for four pyridine dicarboxylic acids, namely, dipicolinic monohydrate, dinicotinic, cinchomeronic and quinolinic. In these acids, the N—$H_{carboxy}$ distances ranged from 0.89 (4) to 2.17 (6) Å, while the C—N—C_{ring} angles ranged from 116.8 (4) to 125.3 (2)°. Although corresponding data obtained subsequently for isonicotinic acid (pyridine-4-carboxylic acid) (Takusagawa & Shimada, 1976) conform well to that correlation, those for both nicotinic acid (pyridine-3-carboxylic acid) (Kutoglu & Scheringer, 1983) and the present compound do not. It thus appears that the degree of correlation shown initially was largely fortuitous.

All bond distances and angles within the quinoline core, the carboxy group and the phenyl group fall within the normal ranges. The mean deviation of the quinoline core atoms from the least-squares best-fit plane through them is 0.022 (3) Å, the maximum deviation being 0.040 (3) Å for atom C(7). For the phenyl group, the corresponding mean deviation is 0.004 (3) Å, the maximum deviation being 0.006 (3) Å for atom C(13). The dihedral angle between these two planes is 37.0 (1)°. The dihedral angle between the best-fit quinoline plane and the carboxy group plane is 53.6 (1)°.

Apart from the hydrogen bonding, four of the five closest approaches between molecules in this structure are between the carboxy H atom, H(1), of one molecule and atoms H(17), C(2), C(9) and C(17) of two other molecules; the fifth close approach occurs between atom O(1) and an H(17) atom. These five approach distances are all at least 0.12 Å less than the sums of the corresponding van der Waals radii.