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}
O1	0.3148 (5)	1.0665 (2)	0.0832 (2)	0.0697 (7)
O2	0.0372 (4)	0.8621 (2)	0.0368 (2)	0.0669 (6)
O3	0.3641 (3)	0.58438 (15)	0.21396 (14)	0.0457 (4)
O4	0.7310 (3)	0.7407 (2)	0.2047 (2)	0.0564 (5)
N	0.3239 (4)	0.7724 (2)	0.1763 (2)	0.0434 (5)
C1	0.5016 (4)	0.4812 (2)	0.2289 (2)	0.0433 (5)
C2	0.4953 (4)	0.7014 (2)	0.1987 (2)	0.0388 (5)
C3	0.4271 (4)	0.9098 (2)	0.1708 (2)	0.0392 (5)
C4	0.2373 (4)	0.9439 (2)	0.0901 (2)	0.0401 (5)
C5	0.4894 (4)	1.0168 (2)	0.2833 (2)	0.0387 (5)
C6	0.3088 (5)	1.0165 (3)	0.3557 (2)	0.0509 (6)
C7	0.3702 (6)	1.1158 (3)	0.4586 (2)	0.0602 (7)
C8	0.6064 (6)	1.2119 (3)	0.4885 (2)	0.0618 (8)
C9	0.7835 (6)	1.2125 (3)	0.4162 (2)	0.0593 (7)
C10	0.7262 (5)	1.1155 (2)	0.3135 (2)	0.0490 (6)
C11	0.7219 (6)	0.5397 (3)	0.3288 (2)	0.0591 (7)
C12	0.5978 (6)	0.4251 (3)	0.1229 (2)	0.0635 (7)
C13	0.2858 (6)	0.3753 (3)	0.2512 (3)	0.0647 (8)

Table 2. *Selected geometric parameters (Å, °)*

O1—C4	1.290 (3)	N—C3	1.447 (3)
O2—C4	1.210 (3)	C1—C12	1.499 (4)
O3—C2	1.338 (3)	C1—C13	1.504 (3)
O3—C1	1.482 (2)	C1—C11	1.518 (3)
O4—C2	1.212 (3)	C3—C5	1.517 (3)
N—C2	1.357 (3)	C3—C4	1.522 (3)
C2—O3—C1	120.7 (2)	N—C3—C4	110.0 (2)
C2—N—C3	118.7 (2)	C5—C3—C4	109.8 (2)
O4—C2—O3	126.3 (2)	O2—C4—O1	124.2 (2)
O4—C2—N	124.1 (2)	O2—C4—C3	122.6 (2)
O3—C2—N	109.6 (2)	O1—C4—C3	113.2 (2)
N—C3—C5	114.2 (2)		

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CFEO* (Solans, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1093). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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o-Cyanophenol

Colin Beswick,[a] Maciej Kubicki[b] and Penelope W. Codding[c]

[a]*Department of Chemistry, Northwestern University, Evanston, Illinois, USA,* [b]*Laboratory of Crystallography, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland, and* [c]*Departments of Chemistry and of Pharmacology and Therapeutics, University of Calgary, Calgary, Alberta, Canada T2N 1N4. E-mail: mkubicki@plpuam11.amu.edu.pl*

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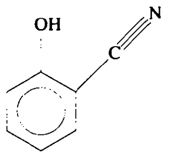
Abstract

O—H···N—C hydrogen bonds connect the two independent molecules of the title compound *o*-hydroxybenzonitrile, C_7H_5NO, into infinite chains. The effects of substituents on endocyclic bond angles are close to additivity.

Comment

The structure of the title compound, (I), was determined as part of a study of hydrogen bonding of donor–acceptor substituted aromatic compounds. There are two independent molecules in the asymmetric unit. The normal probability plot (Abrahams & Keve, 1971; *International Tables for X-ray Crystallography*, 1974) shows that the differences in their geometries are only statistical (the correlation coefficient is 0.98).



(I)

Hydrogen bonds (see Table 3) connect the molecules into *ABAB* chains along the [001] direction. Similar hydrogen-bonding patterns were observed in the structures of *p*-cyanophenol (Higashi & Osaki, 1977) and in 2,6-dibromo-4-cyanophenol (Baughman, Virant & Jacobson, 1981). In both independent molecules, the phenyl rings are strictly planar (within 4σ). The cyano groups are almost coplanar with the ring planes; the angles between the normal to the ring plane and the line C2—C21—N21 are 88.6 (1) and 88.2 (1)° for molecules *A* and *B*, respectively. The planes of the phenyl rings in the two independent molecules make a dihedral angle of 78.80 (5)°.

The pattern of bond lengths is typical; the bond angles, however, are influenced by the presence of the substituents. In their analysis of the influence of the substituents on the geometry of the phenyl ring, Domenicano & Murray-Rust (1979) suggested that this effect is close to additivity for *p*-disubstituted derivatives. They made no estimation for *o*-disubstituted benzenes because steric effects can alter significantly the electronic effects. In the case of *o*-cyanophenol, the steric hindrance is only of little importance; the changes in bond angles should therefore be close to the sums of the changes caused by either substituent alone. This is the case, and the differences between the calculated (assuming additivity) and experimental values of the endocyclic bond angles are equal within 3σ.

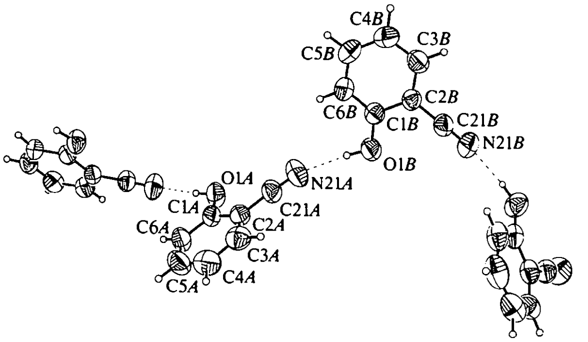


Fig. 1. The hydrogen-bonding network observed in the structure of *o*-cyanophenyl, together with the labelling scheme (Siemens, 1989). The ellipsoids are drawn at the 50% probability level; the H atoms are shown as spheres with an arbitrary radius. The hydrogen bonds are depicted as dashed lines.

Experimental

Commercially available product (Merck) was recrystallized from ethanol.

Crystal data

C_7H_5NO
$M_r = 119.12$
Orthorhombic
Pbca
$a = 7.4614\ (4)$ Å
$b = 16.5571\ (13)$ Å
$c = 20.6129\ (14)$ Å
$V = 2546.5\ (3)$ Å^3
$Z = 16$
$D_x = 1.243$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 15$–$42°$
$\mu = 0.697$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.35 × 0.2 × 0.2 mm
Colourless

Data collection

CAD-4*F* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2617 measured reflections
2617 independent reflections
2048 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 74.91°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 25$
3 standard reflections
frequency: 33 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0401$
$wR(F^2) = 0.1033$
$S = 1.059$
2613 reflections
204 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0097P)^2 + 0.1805P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.12$ e Å^{-3}
$\Delta\rho_{\min} = -0.11$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0032 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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}
C1*A*	0.3712 (2)	0.15233 (8)	0.45686 (6)	0.0591 (4)
O1*A*	0.1934 (2)	0.13825 (7)	0.45800 (5)	0.0742 (3)
C2*A*	0.4352 (2)	0.20816 (8)	0.41163 (6)	0.0581 (4)
C21*A*	0.3100 (2)	0.24713 (9)	0.36946 (7)	0.0662 (4)
N21*A*	0.2114 (2)	0.27747 (9)	0.33529 (7)	0.0910 (5)
C3*A*	0.6173 (3)	0.22489 (10)	0.40651 (8)	0.0704 (5)
C4*A*	0.7365 (3)	0.18590 (12)	0.44606 (10)	0.0848 (5)
C5*A*	0.6736 (3)	0.13118 (13)	0.49100 (10)	0.0865 (6)
C6*A*	0.4943 (3)	0.11420 (11)	0.49680 (8)	0.0739 (5)
C1*B*	0.0458 (2)	0.43694 (8)	0.23802 (6)	0.0521 (3)
O1*B*	0.1081 (2)	0.36246 (6)	0.22411 (5)	0.0694 (3)
C2*B*	0.0137 (2)	0.48903 (8)	0.18646 (6)	0.0524 (3)
C21*B*	0.0512 (2)	0.46223 (9)	0.12180 (7)	0.0614 (4)
N21*B*	0.0826 (2)	0.44162 (9)	0.07051 (6)	0.0830 (5)
C3*B*	−0.0494 (2)	0.56686 (9)	0.19734 (8)	0.0631 (4)
C4*B*	−0.0799 (2)	0.59296 (10)	0.25970 (8)	0.0688 (4)
C5*B*	−0.0489 (2)	0.54090 (10)	0.31066 (7)	0.0672 (4)
C6*B*	0.0137 (2)	0.46420 (10)	0.30064 (7)	0.0608 (4)

Table 2. *Selected geometric parameters (Å, °)*

C1*A*—O1*A*	1.347 (2)	C1*B*—O1*B*	1.349 (2)
C1*A*—C6*A*	1.386 (2)	C1*B*—C6*B*	1.388 (2)
C1*A*—C2*A*	1.397 (2)	C1*B*—C2*B*	1.390 (2)
C2*A*—C3*A*	1.391 (2)	C2*B*—C3*B*	1.390 (2)
C2*A*—C21*A*	1.430 (2)	C2*B*—C21*B*	1.432 (2)
C21*A*—N21*A*	1.136 (2)	C21*B*—N21*B*	1.135 (2)
C3*A*—C4*A*	1.368 (3)	C3*B*—C4*B*	1.375 (2)
C4*A*—C5*A*	1.378 (3)	C4*B*—C5*B*	1.378 (2)
C5*A*—C6*A*	1.372 (3)	C5*B*—C6*B*	1.369 (2)
O1*A*—C1*A*—C6*A*	124.3 (2)	O1*B*—C1*B*—C6*B*	123.68 (12)
O1*A*—C1*A*—C2*A*	117.58 (13)	O1*B*—C1*B*—C2*B*	117.67 (11)
C6*A*—C1*A*—C2*A*	118.1 (2)	C6*B*—C1*B*—C2*B*	118.65 (13)
C3*A*—C2*A*—C1*A*	121.10 (15)	C1*B*—C2*B*—C3*B*	120.69 (12)
C3*A*—C2*A*—C21*A*	120.15 (15)	C1*B*—C2*B*—C21*B*	119.04 (12)
C1*A*—C2*A*—C21*A*	118.7 (2)	C3*B*—C2*B*—C21*B*	120.24 (13)
N21*A*—C21*A*—C2*A*	179.1 (2)	N21*B*—C21*B*—C2*B*	179.2 (2)
C4*A*—C3*A*—C2*A*	119.7 (2)	C4*B*—C3*B*—C2*B*	119.88 (14)
C3*A*—C4*A*—C5*A*	119.3 (2)	C3*B*—C4*B*—C5*B*	119.22 (15)
C6*A*—C5*A*—C4*A*	121.7 (2)	C6*B*—C5*B*—C4*B*	121.50 (14)
C5*A*—C6*A*—C1*A*	120.1 (2)	C5*B*—C6*B*—C1*B*	120.06 (14)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···N21*B*^{i}	0.92 (2)	1.88 (2)	2.795 (2)	173 (2)
O1*B*—H1*B*···N21*A*	0.91 (2)	1.90 (2)	2.798 (2)	172 (2)

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

Data collection: CAD-4*F*. Cell refinement: CAD-4*F*. Data reduction: *ENPROC* (Rettig, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: Stereochemical Workstation (Siemens, 1989). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1277). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2′,3′-Dideoxy-3′-nitrothymidine and 2′-Propoxy-3′-nitrothymidine

Stephen Neidle,[a] Jyoti P. Chattopadhyaya,[b] Nafizal Hossain[b] and Alexander Papchikhin[b]

[a]*CRC Biomolecular Structure Unit, The Institute of Cancer Research, Cotswold Road, Sutton, Surrey SM2 5NG, England, and* [b]*Department of Bioorganic Chemistry, University of Uppsala, Box 581, Biomedical Center, S-751 23 Uppsala, Sweden. E-mail: steve@iris5.icr.ac.uk*

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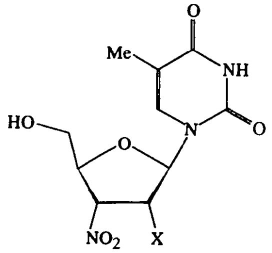
Abstract

The crystal structures of 2′,3′-dideoxy-3′-nitrothymidine, $C_{10}H_{13}N_3O_6$ and 2′-propoxy-3′-nitrothymidine, $C_{13}H_{19}N_3O_7$, are reported. Both compounds are analogous to the anti-HIV nucleoside 3′-azido-2′,3′-dideoxythymidine (AZT). The replacement of the azido group in AZT by the nitro group in these two compounds has resulted in a sugar pucker preference of C2′-*endo* type, as observed in both structures, AZT itself and several of its derivatives.

Comment

A number of modified nucleosides have established antiviral and/or anticancer activity arising from their mis-incorporation into DNA or RNA during replication or transcription. In particular, nucleosides lacking a hydroxyl group at the 3′ position can have activity against human immunodeficiency virus (HIV) by acting as inhibitors of the viral reverse transcriptase enzyme which transcribes viral RNA into DNA. AZT, 3′-azido-2′,3′-dideoxythymidine, is an effective inhibitor which is in current clinical use with HIV patients. The title compounds, 2′,3′-dideoxy-, (I) and 2′-propoxy-3′-nitrothymidine, (II), were synthesised (Hossain, Papchikhin, Garg, Fedorov, & Chattopadhyaya, 1993) as part of an attempt to develop new and more effective reverse transcriptase inhibitors. In this paper, we examine their conformational features, and compare them with those of AZT itself.



(I) $X = H$
(II) $X = OCH_2CH_2CH_3$

Compound (I) is the 3′-nitro analogue of AZT. It has two molecules in the asymmetric unit (Fig. 1). These have distinct conformations about the glycosidic bond with glycosidic angles [O4′—C1′—N1—C2 (χ)] of −172.4 (4)° and −127.1 (4)° for molecules *A* and *B*, respectively. The values for the exocyclic torsion angle [C3′—C4′—C5′—O5′ (γ)] are dissimilar with molecule *A* having a *trans* conformation [174.4 (4)°] and molecule *B* being *gauche*(+) with a torsion angle of 53.0 (6)°. The deoxyribose sugar rings have similar puckers, molecules *A* and *B* having phase angles of pseudorotation *P* (Neidle, 1994) of 202.5 (6)° and 169.6 (6)°, respectively. These correspond to C3′-*exo* and C2′-*endo* sugar puckers, respectively. Compound (II), the 2′-propoxy derivative of (I), has the propyl group in an extended conformation, oriented on the *endo* side of the sugar. Other conformational features of compound (II) include a glycosidic torsion angle of −121.1 (4)°, a pseudorotation phase angle of 140.9 (4)° for the ribose ring (C1′-*exo*/C2′-*endo* pucker) and a C4′—C5′ exocyclic torsion angle of 50.6 (5)°, *i.e* in the *gauche*(+) range.