N2—N1—C3	113.7 (2)	N2′—N1′—C3′	113.0 (2)
C1—N2—N1	107.6 (3)	C1′—N2′—N1′	107.9 (3)
N2—C1—C6	120.5 (3)	N2′—C1′—C6′	122.2 (3)
N2—C1—C2	114.5 (3)	N2′—C1′—C2′	113.8 (3)
C6—C1—C2	125.0 (3)	C6′—C1′—C2′	124.0 (3)
C1—C2—C3	103.3 (3)	C1′—C2′—C3′	102.8 (3)
N1—C3—C14	112.3 (3)	N1′—C3′—C14′	114.5 (3)
N1—C3—C2	100.7 (3)	N1′—C3′—C2′	101.2 (2)
C14—C3—C2	114.1 (3)	C14′—C3′—C2′	111.1 (3)
O1—C4—N1	119.2 (3)	O1′—C4′—N1′	118.8 (3)
O1—C4—C5	123.3 (4)	O1′—C4′—C5′	123.2 (3)
N1—C4—C5	117.5 (4)	N1′—C4′—C5′	118.0 (3)
C7—C6—C1	124.8 (3)	C7′—C6′—C1′	122.9 (3)
C6—C7—C8	127.2 (3)	C6′—C7′—C8′	127.6 (3)
C9—C8—C13	116.9 (3)	C13′—C8′—C9′	118.3 (3)
C9—C8—C7	123.5 (3)	C13′—C8′—C7′	119.2 (3)
C13—C8—C7	119.6 (3)	C9′—C8′—C7′	122.5 (3)
C10—C9—C8	121.3 (4)	C10′—C9′—C8′	120.6 (4)
C11—C10—C9	120.8 (4)	C11′—C10′—C9′	120.3 (4)
C12—C11—C10	118.9 (4)	C12′—C11′—C10′	119.8 (4)
C11—C12—C13	120.7 (4)	C11′—C12′—C13′	120.1 (4)
C12—C13—C8	121.3 (4)	C12′—C13′—C8′	120.8 (4)
C15—C14—C19	117.9 (3)	C15′—C14′—C19′	117.9 (4)
C15—C14—C3	121.3 (3)	C15′—C14′—C3′	119.7 (3)
C19—C14—C3	120.8 (3)	C19′—C14′—C3′	122.0 (3)
C14—C15—C16	121.7 (3)	C14′—C15′—C16′	120.9 (4)
C17—C16—C15	119.3 (4)	C17′—C16′—C15′	120.0 (5)
C18—C17—C16	120.1 (5)	C16′—C17′—C18′	119.9 (5)
C17—C18—C19	120.2 (4)	C17′—C18′—C19′	120.4 (5)
C14—C19—C18	120.8 (4)	C18′—C19′—C14′	120.8 (4)
N1—C3—C14—C15	62.8 (4)	N1′—C3′—C14′—C15′	155.9 (3)
C2—C3—C14—C15	−50.9 (4)	C2′—C3′—C14′—C15′	−90.1 (4)
N1—C3—C14—C19	−117.9 (4)	N1′—C3′—C14′—C19′	−31.5 (4)
C2—C3—C14—C19	128.3 (4)	C2′—C3′—C14′—C19′	82.4 (4)

All H atoms were located experimentally from the final difference Fourier map and refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

RVK thanks the CSIR (India) for financial support in the form of a Senior Research Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1064). Services for accessing these data are described at the back of the journal.

References

El-Hashash, M. A., Soiman, F. M. A., Souka, L. M. & Salman, A. S. S. (1995). *Rev. Roum. Chim.* **40**, 59–66.

Enraf–Nonius (1985). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Vijayabaskar, V. (1997). PhD thesis, Madurai Kamaraj University, India.

Wang, Z.-Y., Shi, H.-J. & Shi, H.-X. (1995). *Hecheng Huaxue*, **3**, 226–230.

Acta Cryst. (1998). C**54**, 978–980

7-Methoxy-2,2,4-trimethyl-1,2-dihydroquinoline

DUNCAN GRAHAM AND ALAN R. KENNEDY

Department of Pure & Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland. E-mail: a.r.kennedy@ccsun.strath.ac.uk

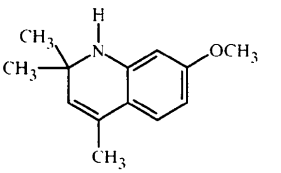
(*Received 10 October 1997; accepted 26 January 1998*)

Abstract

The title compound, $C_{13}H_{17}NO$, was prepared using a new class of activator, alkyl bromides. The heterocyclic ring adopts a non-planar conformation, which contrasts with the conformations found for related compounds.

Comment

The exact structure of substituted dihydroquinolines has been the subject of many previous studies. Originally, the structures of such compounds were incorrectly described as simple Schiff bases of acetone (Knoevenagel, 1921). The currently accepted structures were proposed independently on chemical grounds by Reddelien & Thurm (1932), Cliffe (1933) and Murray *et al.* (1933), but it was not until 1965 that the title compound, (I), was first reported (Rosowsky & Modest, 1965). Starting with *m*-anisidine and acetone, with iodine as an activator, yielded (I) as a single product. Although two isomers are possible, the conformation of the isomer produced was identified from NMR shift data.



(I)

We produced (I) whilst attempting to synthesize alkylated anisidine by refluxing 6-bromohexan-1-ol with *m*-anisidine in petroleum ether and acetone. Compound (I) was isolated as the only major product. Alkyl bromides have not been reported previously as activators in this reaction. Confirmation that this was the previously reported isomer was obtained by crystal structure analysis.

The molecular structure, shown in Fig. 1, contains a bicyclic nucleus with typical shortenings of the C3—C4 and N1—C5 distances due to conjugation effects [C3—C4 1.469 (3), N1—C5 1.381 (2) and N1—C1 1.459 (3) Å]. Similarly substituted heterocyclic fragments adopt one of two conformations. In 6-ethoxy-

8-nitro-2,2,4-trimethyl-1,2-dihydroquinoline (Bonnett *et al.*, 1979), the heterocyclic ring is coplanar with the aromatic ring and the internal bond angle at N1 is 127.0 (4)°. A similar planar conformation is found for the related 2,2-phenyl-substituted compounds of Cardellini *et al.* (1994). However, in three similar structures with aryl ring substituents at the 6-position only (Bonnett *et al.*, 1979; Obodovskaya *et al.*, 1985, 1990), the heterocyclic ring is puckered (C1 being furthest from the plane) and the angle subtended by N1 is less than 120°. Compound (I) does not conform to either group. It has an enlarged C1—N1—C5 angle of 122.6 (2)° but, as the torsion angles of Table 1 show, is non-planar. Deviations from the least-squares plane defined by atoms C4–C9 are N1 0.109 (2), C1 −0.374 (2), C2 −0.106 (2), C3 0.039 (2), C4 −0.004 (2) and C5 0.006 (2) Å.

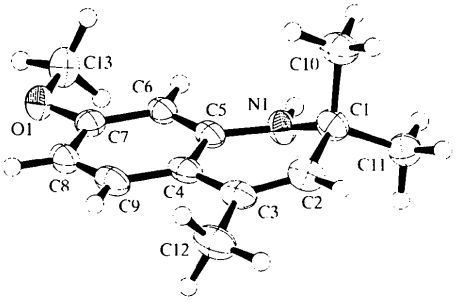


Fig. 1. *ORTEP*II (Johnson, 1976) view of (I) with non-H atoms drawn as 50% probability ellipsoids. H atoms are shown as small spheres of arbitrary radii.

The closest intermolecular contact involves N—H and O, but the geometry [O1···H1^{i} 2.37, O1···N1^{i} 3.133 (2) Å and O1···H1^{i}—N1^{i} 148.6°; symmetry code: (i) $-\frac{1}{2}+x, \frac{1}{2}-y, 2-z$] does not indicate a significant hydrogen-bond interaction.

Experimental

m-Anisidine (2.09 g, 13.66 mmol) was dissolved in a mixture of 20 ml petroleum ether (333–353 K) and 20 ml acetone containing diisopropylethylamine (2.94 g, 22.78 mmol). Then 6-bromohexan-1-ol (0.82 g, 4.55 mmol) was added, and the mixture was refluxed for 16 h. Once the reaction was complete (thin-layer chromatography, CCl_2H_2/MeOH 9:1), the solvent was removed and the residue dissolved in EtOAc. The organic phase was washed (saturated KCl solution × 3) and dried (Na_2SO_4), and the product isolated by wet flash column chromatography (eluant dichloromethane/methanol 20:1) to give a yellow solid, which was recrystallized from ethanol to give colourless crystals of (I).

Crystal data

$C_{13}H_{17}NO$
M_r = 203.28
Orthorhombic
$P2_12_12_1$
a = 8.483 (1) Å
b = 19.174 (3) Å
c = 7.1793 (8) Å
V = 1167.8 (2) Å^3
Z = 4
D_x = 1.156 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 20 reflections
θ = 6.95–9.15°
μ = 0.073 mm^{-1}
T = 123 K
Plate
0.40 × 0.40 × 0.05 mm
Colourless

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2748 measured reflections
2320 independent reflections
1655 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 26.0°
h = −10 → 10
k = −23 → 23
l = −8 → 8
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F
R = 0.036
wR = 0.041
S = 1.220
1655 reflections
154 parameters
Only H atom U's refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: Zachariasen (1968) type 2, Gaussian isotropic
Extinction coefficient: 1.9 (4) × 10^{-6}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

N1—C1	1.459 (3)	C2—C3	1.338 (3)
N1—C5	1.381 (2)	C3—C4	1.469 (3)
C1—C2	1.512 (3)	C4—C5	1.412 (3)
C1—N1—C5	122.6 (2)	C3—C4—C9	124.5 (2)
N1—C1—C2	107.9 (2)	C5—C4—C9	117.8 (2)
C1—C2—C3	123.5 (2)	N1—C5—C4	118.8 (2)
C2—C3—C4	120.1 (2)	N1—C5—C6	120.7 (2)
C3—C4—C5	117.6 (2)	C4—C5—C6	120.4 (2)
N1—C1—C2—C3	−23.6 (3)	C2—C3—C4—C5	9.5 (3)
N1—C5—C4—C3	2.6 (3)	C2—C1—N1—C5	36.7 (3)
C1—C2—C3—C4	2.6 (3)	C6—C7—O1—C13	1.0 (3)
C1—N1—C5—C4	−28.2 (3)		

All reflections were collected with their Friedel opposites. The absolute configuration could not be determined. H atoms were fixed at positions found in difference syntheses.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSC/AFCDiffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SIR* (Burla *et al.*, 1989). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

We wish to thank the BBSRC, UK, for funding DG.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1221). Services for accessing these data are described at the back of the journal.

References

Bonnett, R., Charalambides, A. A., Hursthouse, M. B., Malik, K. M. A., Nicolaidou, P. & Sheldrick, G. M. (1979). *J. Chem. Soc. Perkin Trans.* 1, pp. 488–495.

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Cardellini, L., Carloni, P., Damiani, E., Greci, L., Stipa, P., Rizzola, C. & Sgarabotto, P. (1994). *J. Chem. Soc. Perkin Trans.* 2, pp. 769–773.

Cliffe, W. H. (1933). *J. Chem. Soc.* pp. 1327–1331.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Knoevenagel, E. (1921). *Ber. Dtsch Chem. Ges.* **54**, 1722–1730.

Molecular Structure Corporation (1985). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1993). *TEXSAN. Crystal Structure Analysis Package*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Murray, J. T., Short, W. F. & Stansfield, R. (1933). *J. Am. Chem. Soc.* **55**, 2805–2806.

Obodovskaya, A. E., Starikova, Z. A., Ivanov, Y. A. & Pokrovskaya, I. E. (1985). *Zh. Strukt. Khim.* **26**, 93–95.

Obodovskaya, A. E., Starikova, Z. A., Shikhaliev, K. S., Ivanov, Y. A., Shmyreva, Z. V. & Pokrovskaya, I. E. (1990). *Kristallografiya*, **35**, 687–692.

Reddelien, A. & Thurm, A. (1932). *Ber. Dtsch Chem. Ges.* **65**, 1511–1521.

Rosowsky, A. & Modest, E. J. (1965). *J. Org. Chem.* **30**, 1832–1837.

Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

Acta Cryst. (1998). C**54**, 980–982

A (±)-Cyclocytidine Analogue with a Low-*anti* Conformation around the Glycosyl Bond

HIROFUMI OHISHI, HIDEHITO URATA, MASAO AKAGI AND KEN-ICHI TOMITA

Osaka University of Pharmaceutical Sciences, 4-20-1 Nasahara, Takatsuki, Osaka 569-1094, Japan. E-mail: ohishi@oysun01.oups.ac.jp

(*Received 7 August 1997; accepted 6 January 1998*)

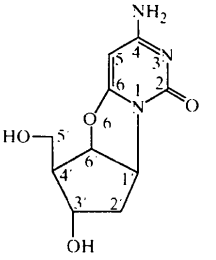
Abstract

The crystal structure of the cytidine analogue (±)-6,6′-anhydro-2′-deoxy-6,6′β-dihydroxycarbacytidine hydrate (alternative name: 3-amino-7-hydroxy-6-hydroxymethyl-6,7,8,8a-tetrahydro-1*H*,5a*H*-cyclopenta[1′,2′:1,2]oxazolo[3,2-*c*]pyrimidin-1-one hydrate), $C_{10}H_{13}N_3O_4.H_2O$, in which the glycosyl torsion angle was fixed by cyclization between the C6′ atom of the cyclopentane ring and the C6 atom of the cytosine base with one O atom, was determined by X-ray analysis. The crystal belongs to the monoclinic space group $P2_1/c$ and the unit cell contains four cytidine analogue and four water molecules. The terminal O5′ atom of the cytidine analogue molecule is hydrogen bonded to a water molecule. The glycosyl torsion angle is low-*anti* (χ = 176.3°) and the puckering of the cyclopentane ring is C3′-envelope.

Comment

Progress in a recent gene analysis has resulted in the discovery of many important genes which cause genetic diseases. In order to inhibit the expression of the target gene, diagnostic and therapeutic antisense application has been developed, which is based on the double-helix formation between a particular mRNA fragment of the target gene and its complementary oligodeoxyribonucleotide analogue. Urata *et al.* (1993) solved by NMR studies the molecular structure of the heterochiral dodecadeoxynucleotide d(CGCGAATTCGCG), which has a single 'chiral defect' at the G4 residue and whose sugar moiety has an unnatural L chirality, and demonstrated that the unnatural G4 residue formed stable Watson–Crick-type base pairing with the natural C9 residue, with *S*-type sugar geometry (C2′-*endo*) and a low-*anti* (χ *ca* 180°) glycosyl conformation in a right-handed B-form duplex. These studies may give a new insight into the chemistry of the antisense application of oligodeoxyribonucleotides having a low-*anti* glycosyl conformation.

As part of the synthesis of oligodeoxyribonucleotide analogues, cyclocarbacytidine, (I), was synthesized by cyclization between the C6 atom of the base and the C6′ atom (adjacent to C1′) of the cyclopentane ring for fixation of the glycosyl torsion angle in the low-*anti* region. This paper deals with the crystal structure analysis of (±)-cyclocarbacytidine.



(I)

An *ORTEP*III (Burnett & Johnson, 1996) drawing of cyclocarbacytidine is shown in Fig. 1, and for comparison, the molecular structure of cytidine determined by Furburg (1951) is shown in Fig. 2. The conformational details are given in Table 1. Normally the glycosyl torsion angle of a nucleoside with an *anti* conformation is in the range *ca* 90 to *ca* 270° [(±)-anticlinal and