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

C1—N11	1.420 (6)	C12—C13	1.485 (6)
C4—N4	1.404 (6)	C13—N13	1.357 (6)
N11—C12	1.298 (6)	C13—C14	1.361 (7)
C12—C14^i	1.432 (7)		
C2—C1—N11	118.9 (5)	N11—C12—C13	116.7 (5)
C6—C1—N11	122.1 (5)	C14^i—C12—C13	116.6 (5)
C3—C4—N4	122.1 (5)	N13—C13—C14	122.8 (5)
C5—C4—N4	120.6 (5)	N13—C13—C12	116.3 (5)
C12—N11—C1	120.5 (4)	C14—C13—C12	120.9 (5)
N11—C12—C14^i	126.6 (5)	C13—C14—C12^i	122.5 (4)

Symmetry codes: (i) $-x, -y, -z$.

The somewhat high R factor is attributed to the limited quality of the available crystals of (1).

Data collection: CAD-4 (Enraf–Nonius, 1980). Cell refinement: CAD-4. Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*93.

We thank EPSRC for support (to DJQ).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1362). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bandrowski, E. (1889). *Monatsh. Chem.* **10**, 123.
Bandrowski, E. (1894). *Chem. Ber.* **27**, 480–486.
Corbett, J. F. (1972). *J. Soc. Cosmet. Chem.* **23**, 683–693.
Cox, H. E. & Lewin, J. U. (1935). *Analyst*, **60**, 350–355.
Crippa, G. B., Bellani, G. & Marubini, A. (1930). *Gazz. Chim. Ital.* **60**, 644–647.
Cunningham, I. D., Wan, N. C. & Cox, B. G. (1994). *J. Chem. Soc. Perkin Trans.* 2, pp. 1849–1853.
Enraf–Nonius (1980). *CAD-4 Operation Software*. Enraf–Nonius, Delft, The Netherlands.
Fan, H. & Wang, Y. (1984). *Zhongguo Yike Daxue Xuebao*, **13**, 55–57.
Feigl, F. & Costa Neto, C. (1956). *J. Soc. Dyers Colour.* **72**, 239–240.
Green, A. G. (1913). *J. Chem. Soc.* pp. 925–933.
Lauer, W. M. & Sunde, C. J. (1939). *J. Org. Chem.* **3**, 261–264.
Povet'eva, Z. P., Chetkina, L. A. & Kopilov, V. V. (1980). *Zh. Strukt. Khim.* **21**, 118–122.
Rice, E. W. (1962). *Anal. Biochem.* **3**, 452–456.
Ritter, J. J. & Schmitz, G. H. (1929). *J. Am. Chem. Soc.* **51**, 1587–1589.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1992). *SHELXTL/PC Users Manual*. Version 4.3. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1993). *HELENA. Program for Data Reduction*. Laboratorium voor Kristal- en Structuurchemie, University of Utrecht, The Netherlands.
Sunde, C. J. & Lauer, W. M. (1952). *J. Org. Chem.* **17**, 609–612.

Acta Cryst. (1996). C**52**, 1776–1779

5′-*O*-Benzoyl-2′,3′-dideoxy-2′-oxo-α-uridine†

CHERAVAKKATTU G. SURESH,[a]* KANDASAMY SAKTHIVEL[b] AND TANMAYA PATHAK[b]

[a]*Division of Biochemical Sciences, National Chemical Laboratory, Pune 411 008, India, and* [b]*Organic Chemistry Division (Synthesis), National Chemical Laboratory, Pune 411 008, India. E-mail: suresh@ncl.ernet.in*

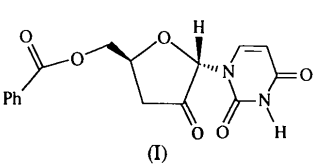
(*Received 11 August 1995; accepted 18 December 1995*)

Abstract

The title compound, 1-(5-*O*-benzoyl-2,3-dideoxy-2-oxo-α-D-ribofuranosyl)-2,4(1*H*,3*H*)-pyrimidinedione, $C_{16}H_{14}N_2O_6$, is an α-nucleoside analogue. The glycosyl torsion angle [O4′—C1′—N1—C2 −76.9 (6)°] has a *syn* conformation. The sugar puckering is O4′-*endo*/C4′-*exo*, with pseudorotation parameters θ_m = 19.8 and P = 61.0. The exocyclic C3′—C4′—C5′—O5′ torsion angle is *gauche–trans* [177.1 (6)°]. The pyrimidine N3 atom forms a hydrogen bond with the O4 atom of a symmetry-related molecule.

Comment

The pharmaceutical applications of nucleosides and nucleoside analogues have been widely recognized (Mitsuya, Yarchoan & Broder, 1990) and molecules like azidothymidine (AZT) are now marketed drugs. These drugs or potential drugs are all β-D-nucleosides and closely resemble the monomers of RNA and DNA. Their anomeric form, however, *i.e.* the α-nucleosides, which are resistant to nuclease digestion, have recently attracted attention as potential antisense drugs (Thuong & Helene, 1993). There are reports on the comparatively more efficient hybridization of modified α-nucleosides to natural DNA and on their high enzymatic stability (Abdel Aleem, Larsen & Pedersen, 1995). We are involved in the synthesis and analysis of α-nucleosides modified at the C2′ and C3′ positions and with various groups attached to the O5′ atom in order to assess the effects of modifications on the overall geometry of the molecule (Sakthivel, Pathak & Suresh, 1994). As part of this study, we report herein the crystal structure of 5′-*O*-benzoyl-2′,3′-dideoxy-2′-oxo-α-uridine, (I).



(I)

† NCL communication No. 6327.

An *ORTEP*II drawing (Johnson, 1976) of (I) together with the atom-labelling scheme is shown in Fig. 1. Bond lengths and angles (Table 2) for the pyrimidine base are as expected (Saenger, 1984). The bond length of the O atom attached to the C2′ position of the sugar corresponds to a double bond, thus confirming the keto form. It is presumably as a result of the influence of this double bond that the neighbouring C3′—C4′ bond is shorter and the furanosyl intra-ring angle at C2′ is wider compared with standard values (Saenger, 1984). A shortening of the exocyclic C4′—C5′ bond is also observed.

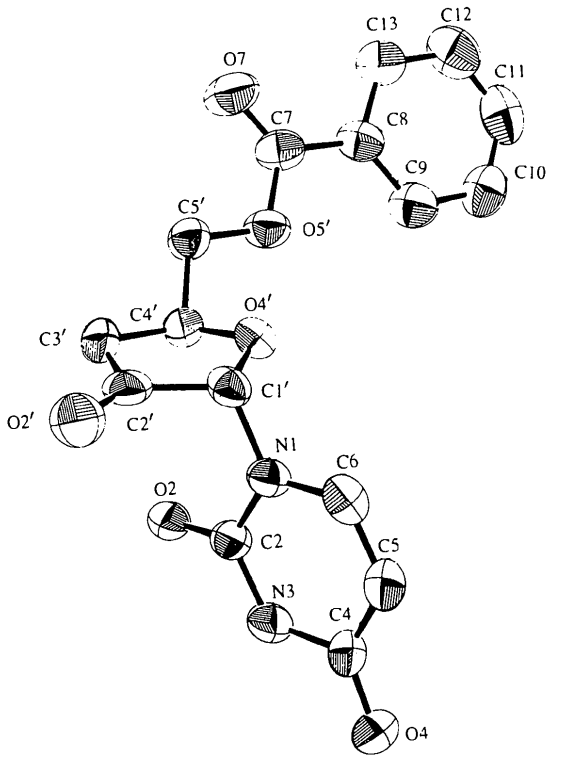


Fig. 1. A perspective view (*ORTEP*II; Johnson, 1976) of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

The pyrimidine base has a *syn* conformation, with a glycosidic torsion angle χ (O4′—C1′—N1—C2) of −76.9 (6)° indicating an α configuration. This is in contrast to the more common *anti* conformation observed in pyrimidine nucleosides (Sundaralingam, 1971). It may be noted that the bulky groups at positions C1′ and C4′, disposed on opposite sides of the furanosyl ring here, are sterically conducive to the *syn* conformation. The sugar puckering is ${}^{0}_{4}T$ (O4′-*endo*/C4′-*exo*) with pseudorotation parameters θ_m and P of 19.8 and 61.0, respectively (Altona & Sundaralingam, 1972). The conformation about the exocyclic C4′—C5′ bond is *gauche–trans*, with a torsion angle γ (C3′—C4′—C5′—O5′) of 177.1 (6)°. The degree of planarity of the three rings is of the order benzene > pyrimidine > furanose and the magnitudes of maximum deviation of atoms from their respective least-squares planes are 0.018, 0.020 and 0.113 Å, respectively. The pyrimidine and furanose planes are almost perpendicular to one another (84.5°), while the plane of the benzene ring makes angles of 63.1 and 60.7°, respectively, with them. The planar *O*-benzoyl group is almost aligned with the C3′—C4′—C5′—O5′ plane (13.5°) and is disposed in a direction opposite to that of the C2′—O2′ keto bond.

The pyrimidine moieties in the crystal are arranged symmetrically about planes parallel to the *ab* plane, bisecting the *c* axis (Fig. 2). The bases are not stacked. The sugar and benzene rings are arranged one above the other on either side of the pyrimidine moieties. There is one hydrogen bond between the heterocyclic N3 atom and the O4 atom of a symmetry-related molecule. Parameters corresponding to this hydrogen bond and other C—H···O-type interactions (Taylor & Kennard, 1982) are listed in Table 3.

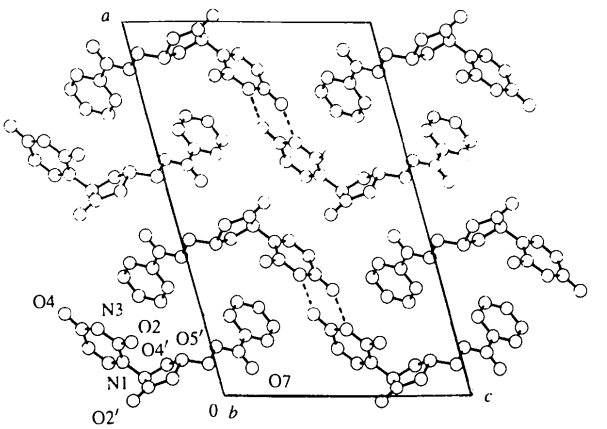


Fig. 2. A packing diagram (*PLUTO*; Motherwell & Clegg, 1978) showing the disposition of bases, sugar and benzene rings in the title structure viewed along the *b* axis. Dotted lines indicate hydrogen bonds.

Experimental

The synthesis of (I) involved the hydrolysis of the corresponding enamine, 1-(2,3-dideoxy-2-*N*-morpholino-5-*O*-trityl-α-D-*glycero*-pent-2-enofuranosyl)uracil, under strongly acidic conditions according to Sakthivel, Pathak & Suresh (1994). A crystal suitable for diffraction analysis was obtained from methanol solution.

Crystal data

$C_{16}H_{14}N_2O_6$
M_r = 330.29
Monoclinic
*C*2
a = 20.337 (3) Å
b = 5.8139 (6) Å
c = 13.362 (2) Å
β = 105.97 (2)°

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 8.32–17.61°
μ = 0.112 mm^{-1}
T = 295 (2) K
Rectangular block

$V = 1519.0(4)$ Å^3
$Z = 4$
$D_x = 1.444$ Mg m^{-3}
0.22 × 0.12 × 0.06 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2235 measured reflections
1249 independent reflections
734 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0463$
$\theta_{max} = 23.47°$
$h = -22 \rightarrow 22$
$k = 0 \rightarrow 6$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0365$
$wR(F^2) = 0.1057$
$S = 0.714$
1249 reflections
273 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.067$
$\Delta\rho_{max} = 0.136$ e Å^{-3}
$\Delta\rho_{min} = -0.200$ 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)
Flack parameter = 0 (3)

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

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

	x	y	z	U_{eq}
O4′	0.0819 (2)	0.3508 (7)	0.8027 (3)	0.0502 (11)
C1′	0.0469 (3)	0.4064 (10)	0.6992 (5)	0.0429 (15)
C2′	0.0217 (3)	0.6508 (12)	0.7031 (5)	0.056 (2)
O2′	−0.0157 (2)	0.7480 (9)	0.6277 (4)	0.0778 (15)
C3′	0.0452 (4)	0.7390 (13)	0.8114 (5)	0.057 (2)
C4′	0.0953 (3)	0.5575 (11)	0.8684 (5)	0.049 (2)
C5′	0.0845 (3)	0.4983 (13)	0.9704 (5)	0.051 (2)
O5′	0.1307 (2)	0.3171 (7)	1.0200 (3)	0.0535 (11)
N1	0.0895 (2)	0.3773 (8)	0.6289 (3)	0.0428 (12)
C2	0.1376 (3)	0.5486 (11)	0.6313 (4)	0.0425 (14)
O2	0.1425 (2)	0.7173 (7)	0.6859 (3)	0.0526 (11)
N3	0.1774 (3)	0.5121 (9)	0.5644 (4)	0.0472 (12)
C4	0.1768 (3)	0.3208 (10)	0.5018 (4)	0.0483 (15)
O4	0.2173 (2)	0.3150 (8)	0.4484 (3)	0.0668 (13)
C5	0.1269 (4)	0.1534 (13)	0.5075 (6)	0.058 (2)
C6	0.0865 (3)	0.1843 (12)	0.5697 (5)	0.052 (2)
C7	0.1173 (3)	0.2316 (12)	1.1053 (4)	0.053 (2)
O7	0.0734 (2)	0.3068 (11)	1.1407 (3)	0.078 (2)
C8	0.1606 (3)	0.0295 (12)	1.1488 (4)	0.0510 (15)
C9	0.2122 (3)	−0.0530 (13)	1.1089 (6)	0.062 (2)
C10	0.2494 (3)	−0.2452 (13)	1.1527 (5)	0.065 (2)
C11	0.2347 (4)	−0.3520 (15)	1.2349 (7)	0.076 (2)
C12	0.1840 (4)	−0.2783 (15)	1.2731 (6)	0.078 (2)
C13	0.1469 (4)	−0.0833 (13)	1.2336 (5)	0.060 (2)

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

O4′—C1′	1.408 (6)	N1—C6	1.365 (8)
O4′—C4′	1.469 (7)	N1—C2	1.391 (7)
C1′—N1	1.452 (7)	C2—O2	1.210 (6)
C1′—C2′	1.517 (9)	C2—N3	1.377 (7)
C2′—O2′	1.221 (7)	N3—C4	1.390 (7)
C2′—C3′	1.485 (10)	C4—O4	1.230 (6)
C3′—C4′	1.518 (9)	C4—C5	1.422 (9)
C4′—C5′	1.480 (8)	C5—C6	1.331 (9)
C5′—O5′	1.446 (7)	C7—O7	1.203 (7)
O5′—C7	1.338 (6)	C7—C8	1.488 (9)
C1′—O4′—C4′	111.1 (4)	C6—N1—C1′	122.1 (5)
O4′—C1′—N1	112.3 (4)	C2—N1—C1′	116.3 (5)
O4′—C1′—C2′	105.4 (5)	O2—C2—N3	123.4 (5)
N1—C1′—C2′	113.5 (5)	O2—C2—N1	122.4 (5)
O2′—C2′—C3′	127.2 (6)	N3—C2—N1	114.2 (6)
O2′—C2′—C1′	123.0 (7)	C2—N3—C4	127.1 (6)
C3′—C2′—C1′	109.6 (6)	O4—C4—N3	118.3 (6)
C2′—C3′—C4′	103.9 (5)	O4—C4—C5	127.9 (6)
O4′—C4′—C5′	108.0 (5)	N3—C4—C5	113.8 (6)
O4′—C4′—C3′	106.3 (5)	C6—C5—C4	120.8 (8)
C5′—C4′—C3′	112.0 (5)	C5—C6—N1	122.4 (7)
O5′—C5′—C4′	110.4 (5)	O7—C7—O5′	123.2 (6)
C7—O5′—C5′	113.7 (4)	O7—C7—C8	123.8 (5)
C6—N1—C2	121.4 (5)	O5′—C7—C8	112.9 (5)
C4′—O4′—C1′—N1	110.3 (5)	C1′—O4′—C4′—C3′	20.1 (6)
C4′—O4′—C1′—C2′	−13.7 (5)	C2′—C3′—C4′—O4′	−17.3 (6)
O4′—C1′—C2′—O2′	−173.8 (5)	O4′—C4′—C5′—O5′	60.4 (6)
N1—C1′—C2′—O2′	63.0 (7)	C3′—C4′—C5′—O5′	177.1 (6)
O4′—C1′—C2′—C3′	2.1 (6)	C4′—C5′—O5′—C7	−170.9 (5)
N1—C1′—C2′—C3′	−121.2 (6)	O4′—C1′—N1—C2	−76.9 (6)
O2′—C2′—C3′—C4′	−174.8 (6)	C5′—O5′—C7—C8	174.0 (5)
C1′—C2′—C3′—C4′	9.6 (7)	O5′—C7—C8—C9	3.7 (8)

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

D—H···A	D···A	D—H···A
N3—H3N···O4^{i}	2.814 (6)	169 (5)
C5′—H5′1···O7^{ii}	3.336 (9)	156 (5)
C6—H6C···O2^{iii}	3.179 (7)	103 (4)
C10—H10C···O4′^{iv}	3.365 (8)	117 (5)
C12—H12C···O4^{v}	3.265 (9)	144 (6)

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (ii) $-x, y, 2-z$; (iii) $x, y-1, z$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, 2-z$; (v) $x, y-1, 1+z$.

The symmetry and lattice type were identified from equivalent reflections and systematic absences. H-atom positions were generated considering ideal geometry and assigned the isotropic displacement parameters of their respective bonding atoms. All H-atom parameters (isotropic) were refined in the subsequent cycles.

Data collection: *CAD-4 PC* (Enraf–Nonius, 1993). Cell refinement: *CAD-4 PC*. Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978).

KS thanks CSIR, New Delhi, for a fellowship. TP is grateful to the Department of Science and Technology, Government of India, for financial support (Grant No. SR/OY/C03/92).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: DE1026). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Abdel Aleem, A. A. H., Larsen, E. & Pedersen, E. B. (1995). *Tetrahedron*, **51**, 7867–7876.

Altona, C. & Sundaralingam, M. (1972). *J. Am. Chem. Soc.* **94**, 8205–8212.

Enraf–Nonius (1993). *CAD-4 PC*. Version 1.2. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Mitsuya, H., Yarchoan, R. & Broder, S. (1990). *Science*, **249**, 1533–1544.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. University of Cambridge, England.
Saenger, W. (1984). In *Principles of Nucleic Acid Structure*. New York: Springer-Verlag.
Sakthivel, K., Pathak, T. & Suresh, C. G. (1994). *Tetrahedron*, **50**, 13251–13260.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sundaralingam, M. (1971). *J. Am. Chem. Soc.* **93**, 6644–6647.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
Thuong, N. T. & Helene, C. (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 666–690.

Acta Cryst. (1996). C**52**, 1779–1780

3,3-Dichloro-4-(*p*-methoxyphenyl)-1-phenyl-2-azetidinone

FILIZ ERCAN,[a]* DINÇER ÜLKÜ[a] AND VILDAN GÜNER[b]

[a]*Hacettepe University, Department of Engineering Physics, 06532 Beytepe, Ankara, Turkey, and* [b]*Hacettepe University, Department of Chemistry, 06532 Beytepe, Ankara, Turkey. E-mail: filiz@eti.cc.hun.edu.tr*

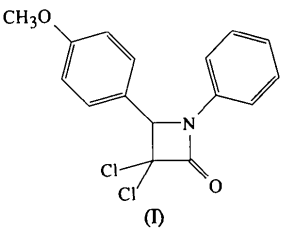
(*Received 16 October 1995; accepted 12 February 1996*)

Abstract

The structure of the title compound consists of discrete $C_{16}H_{13}Cl_2NO_2$ molecules with a closest intermolecular contact of 2.54 (3) Å between the carbonyl O atom and a methyl H atom. The four-membered ring is nearly planar, with long C—C distances of 1.564 (5) and 1.537 (5) Å, similar to the distances observed in other substituted monocyclic β-lactams. The dihedral angle between the planes of the phenyl rings is 78.6 (1)°.

Comment

Many monocyclic β-lactams are reported to show antibiotic as well as antifungal activity (Chambers & Doedens, 1980). Structural information may provide some explanation for such behaviour. The molecular structure of 3,3-dichloro-4-(*p*-methoxyphenyl)-1-phenyl-2-azetidinone, (I), has been determined and the results are presented here.



(I)

The four-membered ring of (I) is nearly planar; deviations from the mean plane are C2 −0.018 (4), C3 0.016 (4), C4 −0.016 (3) and N1 0.019 (3) Å (Fig. 1). While the distances within the four-membered ring are in the range of previously observed minimum (1.342 Å) and maximum (1.602 Å) values for other substituted monocyclic 2-azetidinones (Paulus, Kobelt & Jensen, 1969; Parthasarathy, 1970; Kartha & Ambady, 1973; Colens, Declercq, Germain, Putzeys & Van Meerssche, 1974; Chambers & Doedens, 1980), the ring angle at C3, with a value of 86.3 (2)°, is slightly outside the range of 85.4–85.6° observed previously. The long C3—C4 distance [1.564 (5) Å] reported here seems to be in agreement with those found in similar molecules. The phenyl rings have unexceptional geometry. Their least-squares planes are almost perpendicular to one another [dihedral angle 78.6 (1)°]. The shortest intermolecular distance of 2.54 (3) Å is between the carbonyl O atom and a methyl H atom.

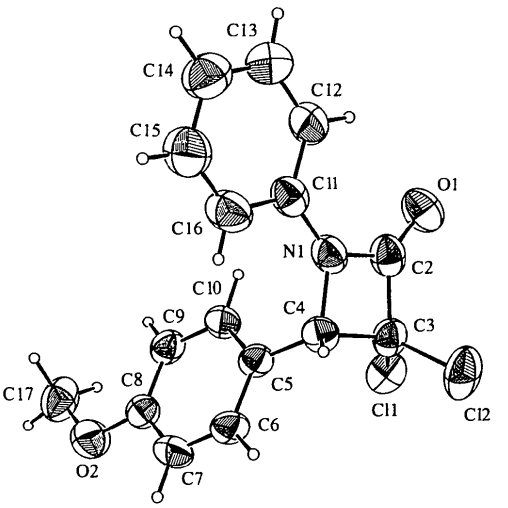


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title molecule with the atom-numbering scheme. Displacement ellipsoids are shown at 50% probability levels.

Experimental

A solution of *p*-methoxybenzylideneaniline (0.01 mol, 2.11 g) and triethylamine (0.02 mol, 2.78 ml) in 35 ml benzene was stirred for 15 min. Dichloroacetyl chloride (0.02 mol, 1.92 ml) was added dropwise to the solution and the mixture stirred at