Absorption correction: empirical
$T_{\min}$ = 0.830, $T_{\max}$ = 1.465
2563 measured reflections
2563 independent reflections
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 38$
$l = 0 \rightarrow 6$
3 standard reflections
frequency: 60 min
intensity variation: <1.5%

Refinement

Refinement on F
R = 0.0514
wR = 0.0525
S = 3.1
1960 reflections
165 parameters
Only H-atom U's refined (one $U_{\rm eq}$ for all H atoms)
Unit weights applied
$(\Delta/\sigma)_{\max}$ = 0.01
$\Delta\rho_{\max}$ = 0.2 e Å^{-3}
$\Delta\rho_{\min}$ = −0.3 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 6 (1)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99-101)

The structure was solved using direct methods and successive Fourier maps (*SHELXS*86; Sheldrick, 1986), and refined using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). H atoms were located from difference Fourier syntheses.

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

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

	x	y	z	$U_{\rm eq}$
S(1)	0.4028 (2)	0.21970 (4)	0.1531 (2)	0.0537
Cl(1)	−0.2507 (2)	0.03670 (4)	−0.3126 (2)	0.0587
C(1)	0.2760 (6)	0.0488 (1)	−1.0692 (8)	0.0484
C(2)	0.0993 (5)	0.1104 (1)	−0.6721 (7)	0.0393
C(3)	−0.1115 (5)	0.1075 (1)	−0.7666 (8)	0.0476
C(4)	−0.2128 (6)	0.1438 (1)	−0.6933 (9)	0.0545
C(5)	−0.1580 (5)	0.1526 (1)	−0.4277 (9)	0.0499
C(6)	0.0519 (5)	0.1572 (1)	−0.3426 (7)	0.0377
C(7)	0.1707 (5)	0.1368 (1)	−0.4607 (7)	0.0365
C(8)	0.3635 (5)	0.1428 (1)	−0.3656 (8)	0.0474
C(9)	0.3019 (5)	0.1863 (1)	−0.0823 (7)	0.0405
C(10)	0.2044 (6)	0.2379 (1)	0.2547 (9)	0.0536
N(1)	0.2083 (6)	0.0276 (1)	−1.2702 (7)	0.0592
N(2)	0.4583 (5)	0.0534 (1)	−0.9780 (8)	0.0616
N(3)	0.1512 (5)	0.0666 (1)	−0.9619 (6)	0.0475
N(4)	0.2208 (4)	0.09129 (9)	−0.7617 (6)	0.0431
N(5)	0.4306 (5)	0.1677 (1)	−0.1799 (7)	0.0513
N(6)	0.1161 (4)	0.18181 (9)	−0.1501 (6)	0.0405

Table 2. *Geometric parameters* (Å, °)

S(1)—C(9)	1.742 (4)	C(4)—C(5)	1.492 (6)
S(1)—C(10)	1.779 (5)	C(5)—C(6)	1.503 (5)
C(1)—N(1)	1.325 (5)	C(6)—C(7)	1.382 (5)
C(1)—N(2)	1.320 (5)	C(6)—N(6)	1.345 (5)
C(1)—N(3)	1.338 (5)	C(7)—C(8)	1.399 (5)
C(2)—C(3)	1.510 (5)	C(8)—N(5)	1.327 (5)
C(2)—C(7)	1.464 (5)	C(9)—N(5)	1.340 (5)
C(2)—N(4)	1.281 (5)	C(9)—N(6)	1.329 (4)
C(3)—C(4)	1.500 (6)	N(3)—N(4)	1.385 (4)
C(10)—S(1)—C(9)	102.9 (2)	N(6)—C(6)—C(7)	122.5 (3)
N(2)—C(1)—N(1)	122.4 (4)	C(6)—C(7)—C(2)	122.1 (3)
N(3)—C(1)—N(1)	117.2 (4)	C(8)—C(7)—C(2)	122.1 (3)
N(3)—C(1)—N(2)	120.4 (4)	C(8)—C(7)—C(6)	115.8 (3)
C(7)—C(2)—C(3)	117.8 (3)	N(5)—C(8)—C(7)	122.9 (4)
N(4)—C(2)—C(3)	124.8 (3)	N(5)—C(9)—S(1)	112.6 (3)
N(4)—C(2)—C(7)	117.3 (3)	N(6)—C(9)—S(1)	120.8 (3)
C(4)—C(3)—C(2)	112.3 (3)	N(6)—C(9)—N(5)	126.7 (3)
C(5)—C(4)—C(3)	113.2 (4)	N(4)—N(3)—C(1)	117.5 (3)
C(6)—C(5)—C(4)	110.9 (3)	N(3)—N(4)—C(2)	116.7 (3)
C(7)—C(6)—C(5)	120.3 (3)	C(9)—N(5)—C(8)	115.9 (3)
N(6)—C(6)—C(5)	117.2 (3)	C(9)—N(6)—C(6)	116.1 (3)

Molecule (5) was prepared according to a published procedure (Bajnati, Kokel & Hubert-Habart, 1987). 0.5 g of (5) was dissolved in 50 ml of boiling methanol and left to stand at room temperature for 6 d, during which time large crystals formed.

This work was supported by a grant (Contrat Coopératif, Décision 90-24) from the Institut Curie.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71434 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1043]

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Acta Cryst. (1994). C**50**, 291–294

Structure of a Modified Nucleoside, 3′α-Diethylphosphono-3′β-hydroxy-5′-*O*-tritylthymidine

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(*Received* 28 *May* 1993; *accepted* 16 *August* 1993)

Abstract

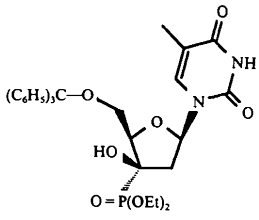
The modified nucleoside of the title was synthesized by nucleophilic addition of lithium diethyl phosphite to the corresponding 3′-keto nucleoside under basic conditions. C—P bond formation resulted from attack on the α face, *trans* to C(5′) and the thymine ring. One molecule of

Acta Crystallographica Section C
ISSN 0108-2701 ©1994

EtOH crystallized with the nucleoside ($C_{33}H_{37}N_2O_8P.$-C_2H_6O). Intermolecular hydrogen bonds were observed between the O atom of the alcohol and the O(3′) hydroxyl H atom, and between the phosphoryl O atom, O(5), and the N(3) H atom of the thymine ring.

Comment

There have been few studies of nucleophilic additions to keto nucleosides (Webb, 1988; Pérez-Pérez, San-Félix, Camarasa, Balzarini & De Clercq, 1992) and most have relied upon NMR studies, particularly NOE experiments, to determine stereochemistry (Bender & Moffett, 1992; Grouiller, Essadiq, Pacheco, Juntunen & Chattopadhyaya, 1985). Our studies on nucleophilic addition of phosphorus reagents to keto nucleosides provided single crystals of one of the synthetic targets, (I); its crystal structure determination allowed the unambiguous assignment of the stereochemistry at C(3′).



(I)

We were particularly interested in the dihedral angle O(3′)—C(3′)—C(4′)—H(4′) that resulted after nucleophilic addition. Therefore, once H(4′) was found on an electron density difference map, further refinements were conducted including this atom. The resulting angle was −158 (4)°.

Surprisingly, the one molecule of ethanol that crystallized was hydrogen bonded only to the hydroxyl H atom, H(O3′), and not to any of the other potential sites. An intermolecular hydrogen bond was also observed between the O(5) atom and the N(3) H atom of the aromatic base, thymine.

Examination of the thymine subunit showed a mean deviation of 0.012 Å from planarity. The thymine ring made a dihedral angle of 92 (1)° with the plane of best fit through the furanose ring.

Experimental

Crystal data

$C_{33}H_{37}N_2O_8P.C_2H_6O$
M_r = 666.7
Monoclinic
$P2_1$
a = 8.651 (4) Å
b = 19.133 (19) Å
c = 10.832 (6) Å
β = 99.76 (4)°

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8-12°
μ = 1.26 mm^{-1}
T = 295 K
Tabular

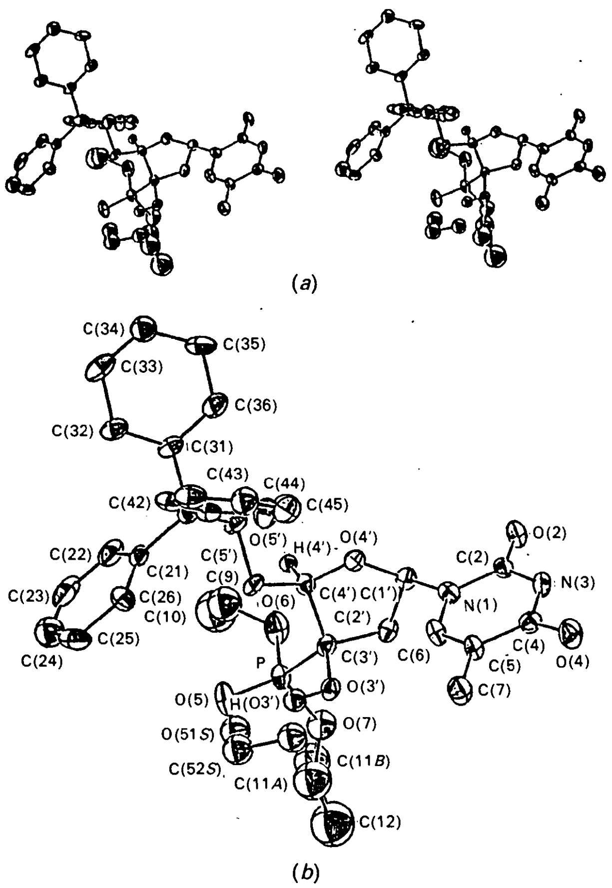


Fig. 1. *ORTEP* (Johnson, 1965) drawings of the title nucleoside: (*a*) a stereoview, (*b*) with atomic labels.

V = 1767 (4) Å^3
Z = 2
D_x = 1.25 Mg m^{-3}

0.55 × 0.16 × 0.10 mm
Clear

Data collection

Enraf-Nonius CAD-4 diffractometer
Profile data from θ-2θ scans
Absorption correction: empirical
$T_{\min}$ = 0.90, $T_{\max}$ = 1.0
4974 measured reflections
3214 independent reflections
1977 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int}$ = 0.033

$\theta_{\max}$ = 25°
h = −10 → 10
k = −22 → 0
l = −12 → 10
3 standard reflections monitored every 200 reflections for orientation standards, every 60 for intensity standards intensity variation: <1.3%

Refinement

Refinement on F
R = 0.066
wR = 0.097
S = 1.14
1977 reflections
381 parameters
$w = 1/[\sigma^2(F) + (0.06F)^2]$

$(\Delta/\sigma)_{\max}$ = 0.19
$\Delta\rho_{\max}$ = 0.43 e Å^{-3}
$\Delta\rho_{\min}$ = −0.12 e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

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}
P	0.1066 (3)	0.0	0.7697 (2)	0.0477 (5)
O(2)	−0.0092 (7)	−0.0485 (4)	1.3441 (5)	0.058 (1)
O(4)	0.4826 (8)	−0.0999 (4)	1.5449 (5)	0.073 (2)
O(5)	0.1773 (8)	−0.0303 (4)	0.6705 (5)	0.072 (1)
O(6)	−0.0722 (7)	0.0073 (5)	0.7403 (5)	0.077 (2)
O(7)	0.163 (1)	0.0770 (4)	0.8100 (7)	0.085 (2)
O(3′)	0.3144 (6)	−0.0578 (3)	0.9437 (4)	0.044 (1)
O(4′)	0.0673 (6)	−0.1360 (3)	1.0392 (5)	0.049 (1)
O(5′)	−0.0013 (6)	−0.2313 (3)	0.8321 (5)	0.051 (1)
O(51*S*)	0.531 (1)	−0.6198 (5)	0.2169 (7)	0.089 (2)
N(1)	0.1753 (8)	−0.0806 (4)	1.2257 (6)	0.049 (1)
N(3)	0.2410 (8)	−0.0753 (4)	1.4417 (5)	0.052 (1)
C(2)	0.1236 (9)	−0.0664 (4)	1.3370 (6)	0.044 (1)
C(4)	0.3925 (9)	−0.0960 (4)	1.4421 (7)	0.048 (2)
C(5)	0.4338 (9)	−0.1075 (5)	1.3233 (7)	0.048 (2)
C(6)	0.328 (1)	−0.0992 (5)	1.2224 (7)	0.051 (2)
C(7)	0.602 (1)	−0.1284 (7)	1.3195 (9)	0.073 (2)
C(8)	0.0327 (9)	−0.2960 (4)	0.7737 (7)	0.049 (2)
C(9)	−0.168 (2)	−0.014 (1)	0.630 (1)	0.12 (5)
C(10)	−0.257 (3)	0.039 (2)	0.564 (2)	0.175 (9)
C(11*A*)	0.291 (5)	0.101 (3)	0.782 (4)	0.15 (1)
C(11*B*)	0.166 (4)	0.132 (2)	0.747 (3)	0.132 (11)
C(12)	0.306 (3)	0.179 (2)	0.771 (2)	0.194 (10)
C(1′)	0.0654 (9)	−0.0736 (4)	1.1112 (7)	0.046 (2)
C(2′)	0.097 (1)	−0.0126 (4)	1.0253 (7)	0.048 (2)
C(3′)	0.1487 (9)	−0.0485 (4)	0.9150 (7)	0.046 (1)
C(4′)	0.0591 (9)	−0.1185 (4)	0.9120 (7)	0.043 (1)
C(5′)	0.1186 (9)	−0.1779 (4)	0.8415 (7)	0.046 (2)
C(21)	0.091 (1)	−0.2793 (4)	0.6519 (7)	0.047 (2)
C(22)	−0.013 (1)	−0.2466 (5)	0.5546 (8)	0.068 (2)
C(23)	0.035 (2)	−0.2302 (6)	0.443 (1)	0.094 (4)
C(24)	0.179 (2)	−0.2445 (8)	0.427 (1)	0.087 (4)
C(25)	0.284 (1)	−0.2723 (5)	0.515 (1)	0.090 (2)
C(26)	0.241 (1)	−0.2917 (5)	0.6356 (8)	0.056 (2)
C(31)	−0.1267 (9)	−0.3348 (4)	0.7508 (8)	0.048 (2)
C(32)	−0.170 (1)	−0.3750 (4)	0.6475 (9)	0.058 (2)
C(33)	−0.317 (1)	−0.4100 (5)	0.630 (1)	0.071 (2)
C(34)	−0.408 (1)	−0.4042 (6)	0.7186 (9)	0.070 (2)
C(35)	−0.363 (1)	−0.3659 (5)	0.825 (1)	0.070 (2)
C(36)	−0.222 (1)	−0.3304 (5)	0.8415 (9)	0.057 (2)
C(41)	0.1420 (9)	−0.3406 (4)	0.8624 (8)	0.049 (2)
C(42)	0.1910 (9)	−0.4064 (4)	0.8256 (8)	0.053 (2)
C(43)	0.285 (1)	−0.4504 (5)	0.915 (1)	0.072 (2)
C(44)	0.326 (1)	−0.4327 (6)	1.030 (1)	0.075 (2)
C(45)	0.273 (1)	−0.3696 (8)	1.073 (1)	0.087 (4)
C(46)	0.182 (1)	−0.3267 (6)	0.9865 (9)	0.071 (2)
C(52*S*)	0.396 (2)	−0.6560 (8)	0.174 (1)	0.094 (4)
C(53*S*)	0.363 (1)	−0.6624 (7)	0.040 (1)	0.085 (2)

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

P—O(5)	1.445 (8)	N(3)—C(2)	1.40 (1)
P—O(6)	1.532 (8)	N(3)—C(4)	1.37 (1)
P—O(7)	1.591 (9)	C(4)—C(5)	1.41 (1)
P—C(3′)	1.81 (1)	C(5)—C(6)	1.31 (1)
O(2)—C(2)	1.21 (1)	C(5)—C(7)	1.51 (2)
O(4)—C(4)	1.25 (1)	C(8)—C(21)	1.53 (1)
O(6)—C(9)	1.39 (2)	C(8)—C(31)	1.55 (1)
O(7)—C(11*A*)	1.28 (6)	C(8)—C(41)	1.50 (1)
O(7)—C(11*B*)	1.26 (5)	C(9)—C(10)	1.39 (3)
O(3′)—C(3′)	1.43 (1)	C(11*A*)—C(12)	1.50 (7)
O(4′)—C(1′)	1.43 (1)	C(11*B*)—C(12)	1.49 (6)
O(4′)—C(4′)	1.41 (1)	C(1′)—C(2′)	1.55 (1)
O(5′)—C(8)	1.44 (1)	C(2′)—C(3′)	1.51 (1)
O(5′)—C(5′)	1.45 (1)	C(3′)—C(4′)	1.54 (1)
O(51*S*)—C(52*S*)	1.37 (2)	C(4′)—C(5′)	1.51 (1)
N(1)—C(2)	1.38 (1)	C(4′)—H(4′)	1.05 (8)
N(1)—C(6)	1.37 (1)	C(52*S*)—C(53*S*)	1.43 (2)
N(1)—C(1′)	1.43 (1)		
O(5)—P—O(6)	114.9 (5)	C(21)—C(8)—C(41)	114.1 (8)
O(5)—P—O(7)	115.2 (6)	C(31)—C(8)—C(41)	106.1 (8)
O(5)—P—C(3′)	113.1 (4)	O(6)—C(9)—C(10)	115 (2)
O(6)—P—O(7)	103.0 (6)	O(7)—C(11*A*)—C(12)	117 (4)
O(6)—P—C(3′)	105.9 (5)	O(7)—C(11*B*)—C(12)	120 (4)
O(7)—P—C(3′)	103.3 (4)	O(4′)—C(1′)—N(1)	109.1 (8)
P—O(6)—C(9)	126 (1)	O(4′)—C(1′)—C(2′)	106.4 (7)
P—O(7)—C(11*A*)	120 (3)	N(1)—C(1′)—C(2′)	115.5 (8)
P—O(7)—C(11*B*)	132 (2)	C(1′)—C(2′)—C(3′)	103.8 (7)
C(1′)—O(4′)—C(4′)	109.4 (7)	P—C(3′)—O(3′)	107.4 (6)
C(8)—O(5′)—C(5′)	116.1 (7)	P—C(3′)—C(2′)	114.3 (7)
C(2)—N(1)—C(6)	121.9 (7)	P—C(3′)—C(4′)	113.6 (6)
C(2)—N(1)—C(1′)	118.1 (7)	O(3′)—C(3′)—C(2′)	107.7 (7)
C(6)—N(1)—C(1′)	120.0 (7)	O(3′)—C(3′)—C(4′)	112.3 (8)
C(2)—N(3)—C(4)	126.9 (7)	C(2′)—C(3′)—C(4′)	101.4 (7)
O(2)—C(2)—N(1)	124.1 (8)	O(4′)—C(4′)—C(3′)	104.1 (7)
O(2)—C(2)—N(3)	123.2 (8)	O(4′)—C(4′)—H(4′)	120 (5)
N(1)—C(2)—N(3)	112.7 (8)	O(4′)—C(4′)—C(5′)	110.5 (8)
O(4)—C(4)—N(3)	118.2 (9)	C(3′)—C(4′)—C(5′)	116.8 (7)
O(4)—C(4)—C(5)	126.0 (9)	C(3′)—C(4′)—H(4′)	104 (5)
N(3)—C(4)—C(5)	115.7 (8)	C(5′)—C(4′)—H(4′)	102 (5)
C(4)—C(5)—C(6)	119.5 (9)	O(5′)—C(5′)—C(4′)	105.5 (7)
C(4)—C(5)—C(7)	117.3 (9)	C(8)—C(21)—C(22)	118.2 (9)
C(6)—C(5)—C(7)	123.2 (9)	C(8)—C(21)—C(26)	122.7 (9)
N(1)—C(6)—C(5)	123.2 (8)	C(8)—C(31)—C(32)	121.1 (9)
O(5′)—C(8)—C(21)	108.8 (8)	C(8)—C(31)—C(36)	118.6 (8)
O(5′)—C(8)—C(31)	103.8 (7)	C(8)—C(41)—C(42)	121.0 (9)
O(5′)—C(8)—C(41)	111.2 (8)	C(8)—C(41)—C(46)	123.5 (9)
C(21)—C(8)—C(31)	112.3 (8)	O(51*S*)—C(52*S*)—C(53*S*)	114 (1)

O(5)—P—O(6)—C(9)	1.37 (130)
O(7)—P—O(6)—C(9)	127.56 (118)
C(3′)—P—O(6)—C(9)	−124.32 (116)
O(5)—P—O(7)—C(11*A*)	−18.71 (218)
O(5)—P—O(7)—C(11*B*)	54.34 (251)
O(6)—P—O(7)—C(11*A*)	−144.71 (212)
O(6)—P—O(7)—C(11*B*)	−71.67 (247)
C(3′)—P—O(7)—C(11*A*)	105.16 (213)
C(3′)—P—O(7)—C(11*B*)	178.20 (244)
O(5)—P—C(3′)—O(3′)	51.85 (61)
O(5)—P—C(3′)—C(2′)	171.23 (58)
O(5)—P—C(3′)—C(4′)	−73.01 (65)
O(6)—P—C(3′)—O(3′)	178.63 (51)
O(6)—P—C(3′)—C(2′)	−61.98 (67)
O(6)—P—C(3′)—C(4′)	53.78 (64)
O(7)—P—C(3′)—O(3′)	−73.40 (58)
O(7)—P—C(3′)—C(2′)	45.98 (68)
O(7)—P—C(3′)—C(4′)	161.75 (58)
P—O(6)—C(9)—C(10)	−120.78 (149)
P—O(7)—C(11*A*)—C(12)	154.44 (206)
P—O(7)—C(11*B*)—C(12)	−136.74 (231)
C(4′)—O(4′)—C(1′)—N(1)	−139.20 (61)
C(4′)—O(4′)—C(1′)—C(2′)	−13.97 (76)
C(1′)—O(4′)—C(4′)—C(3′)	33.18 (73)
C(1′)—O(4′)—C(4′)—C(5′)	159.45 (60)
C(1′)—O(4′)—C(4′)—H(4′)	−82.62 (472)
C(8)—O(5′)—C(5′)—C(4′)	−176.65 (58)
C(6)—N(1)—C(2)—O(2)	178.62 (79)
C(6)—N(1)—C(2)—N(3)	−1.85 (106)
C(1′)—N(1)—C(2)—O(2)	0.23 (118)
C(1′)—N(1)—C(2)—N(3)	179.76 (68)
C(2)—N(1)—C(6)—C(5)	2.64 (129)
C(1′)—N(1)—C(6)—C(5)	−179.00 (82)
C(2)—N(1)—C(1′)—O(4′)	−128.79 (69)
C(2)—N(1)—C(1′)—C(2′)	111.42 (77)
C(6)—N(1)—C(1′)—O(4′)	52.79 (92)
C(6)—N(1)—C(1′)—C(2′)	−67.01 (97)
C(4)—N(3)—C(2)—O(2)	179.12 (79)
C(4)—N(3)—C(2)—N(1)	−0.42 (113)
C(2)—N(3)—C(4)—O(4)	178.71 (80)
C(2)—N(3)—C(4)—C(5)	1.93 (120)
O(4)—C(4)—C(5)—C(6)	−177.68 (90)
O(4)—C(4)—C(5)—C(7)	1.76 (138)
N(3)—C(4)—C(5)—C(6)	−1.19 (120)
N(3)—C(4)—C(5)—C(7)	178.25 (83)
C(4)—C(5)—C(6)—N(1)	−0.95 (134)
C(7)—C(5)—C(6)—N(1)	179.63 (90)
O(4′)—C(1′)—C(2′)—C(3′)	−11.33 (76)
N(1)—C(1′)—C(2′)—C(3′)	109.93 (72)
C(1′)—C(2′)—C(3′)—P	152.06 (52)

C(1′)—C(2′)—C(3′)—O(3′)	−88.69 (68)
C(1′)—C(2′)—C(3′)—C(4′)	29.42 (72)
P—C(3′)—C(4′)—O(4′)	−161.83 (49)
P—C(3′)—C(4′)—C(5′)	75.95 (74)
P—C(3′)—C(4′)—H(4′)	−35.60 (375)
O(3′)—C(3′)—C(4′)—O(4′)	75.98 (69)
O(3′)—C(3′)—C(4′)—C(5′)	−46.23 (82)
O(3′)—C(3′)—C(4′)—H(4′)	−157.78 (372)
C(2′)—C(3′)—C(4′)—O(4′)	−38.71 (71)
C(2′)—C(3′)—C(4′)—C(5′)	−160.93 (63)
C(2′)—C(3′)—C(4′)—H(4′)	87.52 (374)
O(4′)—C(4′)—C(5′)—O(5′)	72.16 (72)
C(3′)—C(4′)—C(5′)—O(5′)	−169.02 (58)
H(4′)—C(4′)—C(5′)—O(5′)	−56.18 (394)

Nucleophilic addition of lithium diethyl phosphite to the sensitive 5′-*O*-trityl-3′-keto-thymidine resulted in a solid product. The product was recrystallized from a mixture of $CHCl_3$ and MeOH with < 1% EtOH. The mixture was heated in a closed vial until the solid disolved completely into solution, whereupon, it was allowed to cool slowly to room temperature. The container lid was then removed and the mixture allowed to stand for approximately 20 h. Clear tabular crystals were then apparent and no solvent remained.

The scan range was $(0.9 + 0.35\tan\theta)^\circ$, the scan speed 0.5–3.3° min^{-1}; the background count was 25% below and above the range, and the ratio of counting time for reflections to background was 2:1. The structure was determined by direct methods. The least-squares procedure refined all non-H atoms anisotropically except for the ethoxy group C atoms, the *para* C atoms of the phenyl groups and the solvent molecule C atoms. A C atom of one ethoxy group appeared to be disordered and was refined as C(11*A*) and C(11*B*) with equal occupancies of 0.5. All H atoms were included in the structure-factor calculations at fixed positions except H(4′), which was included in the least-squares refinement.

The absolute stereochemistry of the ribose ring was known in advance and so no attempt was made to determine absolute configuration from X-ray diffraction data. The scattering factors, f' and f'', were included in the structure-factor calculations. The anomalous scattering factor calculations were expected to be small and the values of R for the two enantiomorph model refinements were not significantly different. The parameters supplied are for the enantiomer which corresponds to the known absolute stereochemistry.

Computer programs used: *MolEN* (Fair, 1990); *ORTEP* (Johnson, 1965).

We thank the National Institutes of Health (GM-44986) for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, least-squares-planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71573 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1082]

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Acta Cryst. (1994). **C50**, 294–297

(*E*)-1,3-Dibenzoyl-2-trifluoromethylpropene and 3-Benzoyl-6-phenyl-2,4-bis(trifluoromethyl)-2*H*-pyran-2-ol: Novel Products from the Oxidation of 1-Phenyl-4,4,4-trifluorobut-2-yn-1-ol with Active Manganese(IV) Oxide

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(*Received* 26 *April* 1993; *accepted* 24 *August* 1993)

Abstract

Comparison of the two benzoyl groups attached to the ends of the propene chain reveals a slight shrinkage in the linking C—C bond when the group is conjugated to the propene double bond [1.490 (7) *cf.* 1.527 (6) Å for the unconjugated group]. However, this is not reflected in the double bond itself, which at 1.312 (7) Å is extremely short. In the substituted pyran, the benzoyl group has been forced out of conjugation by steric congestion [O=C—C=C 91.4 (8)°, linking C—C 1.521 (7) Å] but in this case too, even though the adjacent double bond is able to conjugate within the pyran ring, it still retains full double-bond character [1.328 (8) Å]. Intermolecular hydrogen bonds between the benzoyl O atom and the alcohol group [O—H 0.99 (6), H···O 1.80 (6), O···O 2.738 (6) Å, O—H···O 157 (6)°] link the pyran molecules into infinite chains along *a*.

Comment

The structure determinations reported herein form part of a general investigation of the reactions of alkynes containing the $CF_3C\equiv C$ grouping (Tajammal & Tipping, 1990). The reaction of the alcohol (1) with active MnO_2 was undertaken in an attempt to prepare the corresponding ketone (2); however, (2) proved susceptible to hydrolysis