Trigonal
$P3_2$
a = 9.221 (4) Å
c = 14.006 (6) Å
V = 1031.4 (9) Å^3
Z = 3
D_x = 1.277 Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
θ = 10.2–12.0°
μ = 0.092 mm^{-1}
T = 293 K
Prismatic
0.34 × 0.31 × 0.17 mm
Colourless

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: none
1780 measured reflections
1636 independent reflections
1150 reflections with $I > 2\sigma(I)$

R_{int} = 0.029
θ_{max} = 27.48°
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 18$
3 standard reflections
every 150 reflections
intensity decay: 0.68%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.121
S = 0.926
1636 reflections
172 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.011$
$\Delta\rho_{max}$ = 0.156 e Å^{-3}
$\Delta\rho_{min}$ = −0.161 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C1—C2	1.520 (6)	C2—C3	1.513 (7)
C1—C5	1.566 (5)	C9—C10	1.519 (6)
C1—C10	1.510 (7)		
C2—C1—C5	103.3 (3)	C5—C6—C7	114.4 (3)
C2—C1—C10	115.9 (4)	C6—C7—C8	114.5 (3)
C5—C1—C10	116.5 (3)	C6—C7—C11	103.1 (3)
O3—C3—C2	114.5 (4)	C8—C7—C11	117.3 (3)
O3—C3—C4	110.0 (3)	O8—C8—C7	105.4 (3)
C2—C3—C4	105.1 (3)	O8—C8—C9	109.9 (3)
C1—C5—C4	102.3 (3)	C7—C8—C9	112.5 (3)
C1—C5—C6	108.6 (3)	C7—C11—C12	102.2 (3)
C4—C5—C6	116.1 (3)	C7—C11—C13	117.1 (3)
O6—C6—C5	110.8 (3)	C12—C11—C13	109.4 (4)
O6—C6—C7	103.4 (3)		
O6—C6—C7—C11	−32.3 (4)	C5—C1—C10—C9	38.0 (5)
O6—C12—C11—C7	−12.4 (5)	C5—C6—C7—C8	78.6 (4)
C1—C2—C3—C4	28.8 (4)	C6—O6—C12—C11	−8.6 (5)
C1—C5—C4—C3	−17.3 (4)	C6—C5—C1—C10	39.6 (4)
C1—C5—C6—C7	−91.0 (4)	C6—C7—C8—C9	−54.7 (4)
C1—C10—C9—C8	−89.4 (5)	C6—C7—C11—C12	26.9 (4)
C2—C1—C5—C4	34.6 (4)	C7—C6—O6—C12	25.9 (4)
C2—C3—C4—C5	−6.6 (4)	C7—C8—C9—C10	71.6 (4)
C3—C2—C1—C5	−39.7 (4)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O3—H30···O8^{i}	0.917	1.873	2.739 (5)	156.5
O8—H80···O3^{ii}	0.880	1.912	2.790 (5)	175.3

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - y, x - y, z - \frac{1}{3}$.

All H atoms were obtained from difference Fourier synthesis but not refined. Isotropic displacement parameters of the H atoms were set equal to 1.05U_{eq} of the bonded non-H atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995*b*). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *CHARON* (Lauher, 1989). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1327). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.

Bohlmann, F. & Chen, Z.-L. (1982). *Phytochemistry*, **21**, 2120–2122.

Helal, A. M., Nakamura, N., Meselhy, M. R., El-Fishawy, A. M., Hattori, M. & Mahran, G. H. (1997). *Phytochemistry*, **45**, 551–554.

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

Lauher, J. W. (1989). *CHARON. A Graphics Program for Postscript Printers*. The Research Foundation of the State University of New York, USA.

Molecular Structure Corporation (1995*a*). *MSC/AFC Diffractometer Control Software*. Version 5.3.2c. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1995*b*). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

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

Acta Cryst. (1998). **C54**, 114–116

Diethyl 3,7-Hypoxanthyldiacetate

GEETA SOOD, CARL H. SCHWALBE AND WILLIAM FRASER

Pharmaceutical Sciences Institute, Aston University, Aston Triangle, Birmingham B4 7ET, England. E-mail: c.h.schwalbe@aston.ac.uk

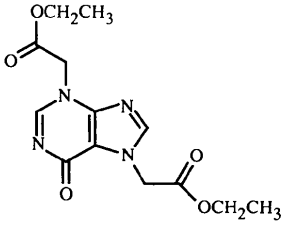
(*Received 4 June 1997; accepted 8 September 1997*)

Abstract

The title compound, diethyl 6-oxo-6,7-dihydro-3*H*-purine-3,7-diacetate, $C_{13}H_{16}N_4O_5$, was obtained by direct alkylation of hypoxanthine using ethyl bromoacetate, in the presence of potassium carbonate; the two alkyl substituents are attached to the heterocycle at positions N3 and N7. Both side chains avoid steric hindrance with the heterocycle, as demonstrated by the torsion angles C2—N3—C15—C16 −68.9 (2) and C8—N7—C10—C11 106.8 (2)°.

Comment

Alkylation of purine bases can result in the attachment of substituents at various positions with regioselectivity influenced by the choice of heterocycle, alkylating agent, additional base, solvent and reaction temperature (Robins *et al.*, 1996; Green *et al.*, 1990). Direct alkylation of adenine (Flensburg & Egholm, 1994) and its homologue 2-aminoadenine (Sood, Schwalbe & Fraser, 1997) can be achieved by using ethyl bromoacetate and sodium hydride in dimethylformamide to give N9-substituted products in good yield with little or none of their corresponding N7 regioisomers. Alkylation of 2,6-dichloropurine (Chan *et al.*, 1995) in acetonitrile using ethyl bromoacetate, but with potassium carbonate as base, results in the formation of a separable mixture of N9- and N7-substituted regioisomers. Under similar conditions, we reacted the purine ring system hypoxanthine with an excess of ethyl bromoacetate to give a mixture of alkylated products, with the major component formed in 61% yield. Spectroscopic analysis indicated the presence of three carbonyl groups; one of each of the two ethyl acetate substituents and the third at C6 of the heterocycle. Further indications were that alkylation had occurred at N3 in the pyrimidine part of the purine ring system and not at O6 (nor at N1). However, it remained unclear at which position, either N9 or N7, the second ethyl acetate substituent had become attached. We undertook the crystal structure determination to establish the substitution pattern of the product. This revealed that the title compound, (1), was indeed the N7 and not the N9 regioisomer. Possible steric clashes between two adjacent ethyl acetate substituents would discourage their attachment at both N3 and N9 or at both O6 and N7 in the same hypoxanthyl derivative. Thus, the regiochemistry of the major dialkylated product, (1), appears to be determined by the site of attachment of the first ethyl acetate fragment.



(1)

A near coplanar arrangement [within ±0.022 (1) Å] of the heterocyclic ring atoms is evident in the crystal structure of (1). The side chains attached at N3 and N7 avoid steric hindrance; the torsion angle C2—N3—C15—C16 is −68.9 (2)° and C8—N7—C10—C11 is more orthogonal at 106.8 (2)°. The C16—O16 bond is marginally shorter than the other ester carbonyl bond. Compared with values averaged between two independent molecules of the 1*H* lactam form of hypoxanthine (Schmalle, Hänggi & Dubler, 1988), the N1—C2 and C6—O6 carbonyl bond lengths are both shorter in (1), by 0.072 (3) and 0.012 (3) Å, respectively, and the internal angles C8—C7—C5, N1—C6—C5 and C2—N3—C4 are expanded in (1), by 2.0 (6), 2.4 (2) and 3.7 (2)°, respectively. Unlike hypoxanthine and its hydrate (Munns & Tollin, 1970; Thewalt, Bugg & Marsh, 1970), nitrate (Rosenstein *et al.*, 1982) and hydrochloride (Sletten & Jensen, 1969) forms, (1) lacks N—H hydrogen-bond donors and therefore displays only an intermolecular contact from C2—H2 to O11: H2···O11^{i} 2.24 (2), C2···O11^{i} 3.177 (2) Å and C2—H2···O11^{i} 153 (1)°; symmetry code: (i) $-x, -y, 1-z$.

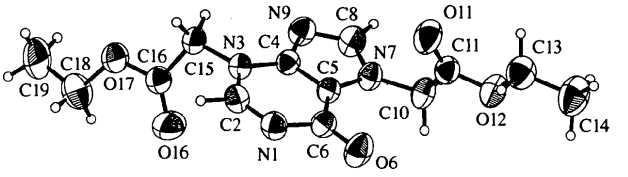


Fig. 1. *ORTEP*II view (Johnson, 1976) of the title molecule. Displacement ellipsoids are shown at the 50% probability level.

Experimental

Potassium carbonate (2.13 g, 47.6 mmol) and ethyl bromoacetate (2.57 g, 48.4 mmol) were added to a solution of hypoxanthine (2.10 g, 15.4 mmol) in dry acetonitrile (30 ml). After stirring for 48 h at room temperature, the product solution was filtered and the solvent evaporated under vacuum. The residue was purified by flash column chromatography on silica, eluting with ethyl acetate–methanol (8:1). Recrystallization from methanol gave the title compound, (1) (2.88 g, 61%, m.p. 412–414 K). TLC (ethyl acetate–methanol 8:1): R_f 0.40. IR (KBr disc): ν_{max} 3120, 3060, 2994, 2940, 1750, 1731, 1700, 1630, 1605, 1550, 1345, 1230, 1020 cm^{-1}. ^{1}H NMR [250.1 MHz; $(CD_3)_2SO$]: δ 1.21 (*t*, 6H, J = 7.1 Hz, 2 × CH_3), 4.13 (*q*, 2H, J = 7.1 Hz, CH_2O), 4.18 (*q*, 2H, J = 7.1 Hz, CH_2O), 4.83 (*s*, 2H, CH_2N), 5.11 (*s*, 2H, CH_2N), 8.11 (*s*, 1H, CH-8), 8.38 p.p.m. (*s*, 1H, CH-2). ^{13}C NMR [62.9 MHz; $(CD_3)_2SO$]: δ 14.2 (CH_3), 44.6 (CH_2O), 47.3 (CH_2O), 61.5 (CH_2N), 61.7 (CH_2N), 122.9 (C-5), 141.8 (C-8), 148.2 (C-6), 149.0 (C-2), 155.9 (C-4), 167.9 (CO), 168.3 p.p.m. (CO). MS (electrospray): *m/z* (I_r) 309 (M + H, 100%). Analysis calculated for $C_{13}H_{16}N_4O_5$: C 50.6, H 5.2, N 18.2%; found: C 50.4, H 5.2, N 17.9%.

Crystal data

$C_{13}H_{16}N_4O_5$
M_r = 308.30
Orthorhombic
Pbca
a = 11.356 (2) Å
b = 13.243 (2) Å
c = 20.002 (3) Å
V = 3008.3 (8) Å^3
Z = 8
D_x = 1.361 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 24.0–36.7°
μ = 0.902 mm^{-1}
T = 293 (2) K
Tabular
0.55 × 0.45 × 0.25 mm
Transparent

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.705, T_{max} = 0.799
7043 measured reflections
3093 independent reflections
2668 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 74.86°
$h = -1 \rightarrow 14$
$k = -16 \rightarrow 16$
$l = -1 \rightarrow 25$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.125
S = 1.057
3093 reflections
264 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 0.4861P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.005$
$\Delta\rho_{max}$ = 0.213 e Å^{-3}
$\Delta\rho_{min}$ = −0.270 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0031 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C2	1.294 (2)	C11—O11	1.197 (2)
C6—O6	1.234 (2)	C16—O16	1.191 (2)
N1—C2—N3	126.74 (14)	C8—N7—C5	106.27 (11)
C2—N3—C4	115.75 (11)	C8—N9—C4	102.80 (11)
N1—C6—C5	114.06 (11)		
C8—N7—C10—C11	106.8 (2)	C2—N3—C15—C16	−68.9 (2)
N7—C10—C11—O12	172.02 (13)	N3—C15—C16—O16	−6.5 (3)
O11—C11—O12—C13	1.8 (2)	C15—C16—O17—C18	−179.5 (2)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *DATREDXL* (Brookhaven National Laboratory & University of Birmingham, 1986). Program(s) used to solve structure: *MULTAN*84 (Main, Germain & Woolfson, 1984). 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.

We thank the Engineering and Physical Sciences Research Council (EPSRC), for a total technology studentship (GS), the EPSRC Mass Spectrometry Service (Swansea), Celltech Therapeutics (Slough), for continuous support of the DNA molecular recognition project, and Mike Eaton and Jim Turner for helpful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1236). Services for accessing these data are described at the back of the journal.

References

Brookhaven National Laboratory & University of Birmingham (1986). *DATREDXL. Program for Data Reduction*. University of Birmingham, England.
Chan, D. M. C., Sood, G., Schwalbe, C. H. & Fraser, W. (1995). *Acta Cryst.* C**51**, 2383–2386.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Flensburg, C. & Egholm, M. (1994). *Acta Cryst.* C**50**, 1480–1482.
Green, G. R., Grinter, T. J., Kincey, P. M. & Jarvest, R. L. (1990). *Tetrahedron*, **46**, 6903–6914.
Johnson. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Germain, G. & Woolfson, M. M. (1984). *MULTAN*84. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.
Munns, A. R. I. & Tollin, P. (1970). *Acta Cryst.* B**26**, 1101–1113.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Robins, M. J., Zou, R. M., Guo, Z. & Wnuk, S. F. (1996). *J. Org. Chem.* **61**, 9207-9212.
Rosenstein, R. D., Oberding, M., Hyde, J. R., Zubieta, J., Karlin, K. D. & Seeman, N. C. (1982). *Cryst. Struct. Commun.* **11**, 1507–1513.
Schmalle, H. W., Hänggi, G. & Dubler, E. (1988). *Acta Cryst.* C**44**, 732–736.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sletten, J. & Jensen, L. H. (1969). *Acta Cryst.* B**25**, 1608–1614.
Sood, G., Schwalbe, C. H. & Fraser, W. (1997). *Acta Cryst.* C**53**, 1624–1626.
Thewalt, U., Bugg, C. E. & Marsh, R. E. (1970). *Acta Cryst.* B**26**, 1089–1101.

Acta Cryst. (1998). C**54**, 116–119

Photochemistry of Triptycene-1,4-quinone

TAI Y. FU, JANET N. GAMLIN, GUNNAR OLOVSSON, JOHN R. SCHEFFER, JAMES TROTTER AND DEAN T. YOUNG

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1. E-mail: jtrt@xray4.chem.ubc.ca

(Received 27 May 1997; accepted 15 September 1997)

Abstract

Photolysis of 9,10-dihydro-9,10[1′,2′]benzenoanthracene-1′,4′-quinone, $C_{20}H_{12}O_2$, in oxygenated acetone gives the novel photoproduct 9,10-dihydro-9,10-ethanoanthracen-11-one-12-spiro-2′-cyclopent-4′-ene-1′, 3′-dione, $C_{20}H_{12}O_3$. The reactant quinone molecule has ideal *mm* symmetry and lies on a crystallographic mirror plane in *Pnma*; the photoproduct molecule has ideal *m* symmetry, which is not utilized in packing in $Pna2_1$. This product is formed only in the presence of oxygen and a mechanism for its formation is proposed. Unreactivity in attempted solid-state photolysis can be rationalized in terms of crystal packing.

Comment

Photolysis of triptycene-1,4-quinone (9,10-dihydro-9,10-[1′,2′]benzenoanthracene-1′,4′-quinone), (1) (Fig. 1), in