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[(3*R*,4*S*,4a*R*,10a*S*)-5,10-Diacetyl-3,4,4a,5,6,7,10,10a-octahydro-8-methoxy-6-oxo-2*H*-pyrano[3,2-*g*]pteridin-3,4-diyl diacetate†

John N. Low,[a] M. Dolores López,[b] M. Luisa Quijano,[b] Adolfo Sánchez[b] and Manuel Nogueras[b]

[a]*AMRC, Department of Applied Physics and Electronic & Mechanical Engineering, University of Dundee, Dundee DD1 4HN, Scotland, and* [b]*Departamento de Quimica Inorganica y Organica, Facultad de Ciencias Experimentales, Universidad de Jaen, 23071-Jaen, Spain. E-mail: j.n.low@dundee.ac.uk*

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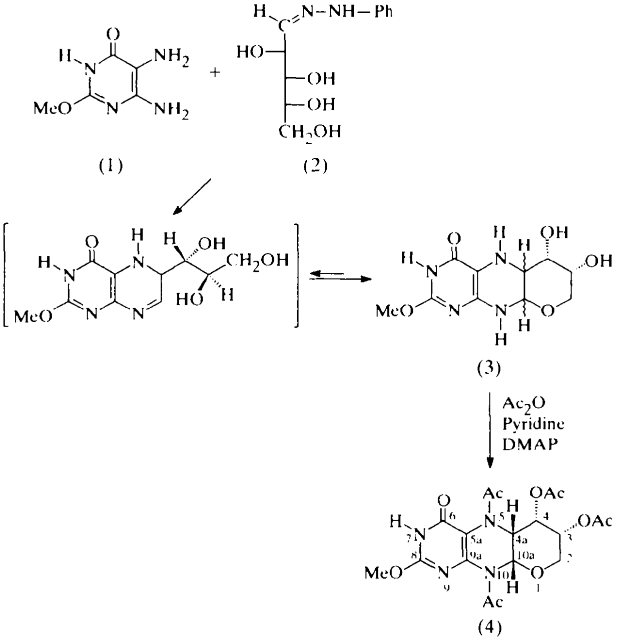
Abstract

The structure and stereochemistry of the title compound, $C_{18}H_{22}N_4O_9$, have been determined. The H atoms at the *A*/*B* ring fusion are in the *cis* position. There is one hydrogen bond in the structure, N7—H7···O51 [N···O 2.886 (4) Å], which links the molecules into infinite chains along the *a* axis.

Comment

In a previous paper (Low *et al.*, 1995), we described the preparation and structure of (3*R*,4*R*,4a*S*,10a*R*)-5-acetyl-3,4,4a,5,6,7,10,10a-octahydro-8-methoxy-7-methyl-6-oxo-2*H*-pyrano[3,2-*g*]pteridin-3,4-diyl diacetate, $C_{17}H_{22}N_4O_8$, (5), which is closely related to the title compound, (4). The present paper thus continues our investigations of the preparation and structural study of compounds formed by the reactions of substituted 5,6-diaminopyrimidines with carbohydrate derivatives.



It was not possible to establish the absolute structure of (4) from the X-ray data, but this was already known from the configuration of the D-arabinose phenylhydrazone used in its synthesis; Fig. 1 and the various data tables all refer to this known configuration. The bond lengths and angles in (4) are in broad agreement with those in (5), and are those expected for this type of molecule (Orpen *et al.*, 1994). Structure (4), like (5), has *cis* H atoms at the *A*/*B* ring fusion and double bonds at C5a═C9a and C8═N9 (Table 1). However, molecules (4) and (5) differ conformationally as expected [in the following discussion the values for (5) are given in square brackets]. The torsion angles N7—C8—N9—C9a, C4—C4a—C10a—O1 and N5—C4a—C10a—N10 are 5.9 (5) [−2.0 (4)], −2.7 (4) [−47.1 (5)] and 2.9 (4)° [−52.0 (5)°], respectively. Ring *A* has a boat conformation (Boeyens, 1978) with the following Cremer & Pople (1975) puckering parameters: Q = 0.755 (3) Å [0.504 (5) Å], θ = 89.8° [6.5 (6)°] and φ = 359.6 (3)° [54 (5)°]. The central *B* ring has a boat conformation, with Q = 0.538 (3) Å [0.481 (5) Å], θ = 86.9 (3)° [125.6 (6)°] and φ = 0.5 (4)° [236.6 (7)°]. The *C* ring is almost planar but is deformed slightly to a skew-boat, with Q = 0.096 (3) Å [0.093 (5) Å], θ =

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† Alternative name: 5,10-diacetyl-3,4,5a,6,7,8,9a,10-octahydro-2-methoxy-4-oxo-5*H*-pyrano[3,2-*g*]pteridin-6,7-diyl diacetate.

78.2 (2)° [108 (3)] and φ = 123 (2)° [324 (3)°], *i.e.* it has a similar conformation to the *C* ring in (5).

In the crystal structure of (4), molecules are linked by an N—H· · ·O hydrogen bond to form infinite chains along the *a* axis (see Table 2).

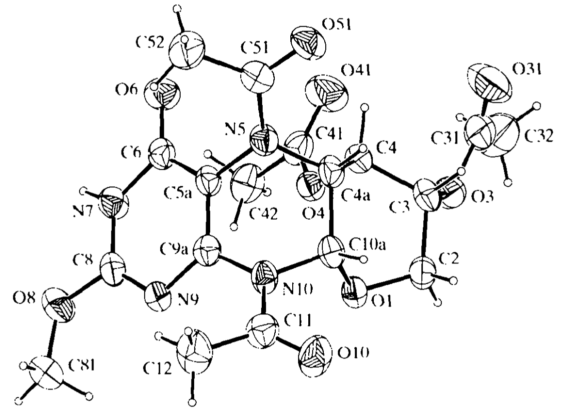

Fig. 1. A view of (4), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level, and only half of the disordered methyl H atoms are included.

Experimental

5,6-Diamino-2-methoxypyrimidin-4(3*H*)-one, (1), and D-arabinose phenylhydrazone, (2), were reacted under the conditions described by Soyka *et al.* (1990). The diastereomic mixture, (3), was isolated in a 65% yield, and converted in 88% yield to its tetraacetyl derivative, (4), for crystal structure analysis.

Crystal data

$C_{18}H_{22}N_4O_9$
M_r = 438.40
Orthorhombic
$P2_12_12_1$
a = 7.941 (3) Å
b = 17.481 (2) Å
c = 14.511 (3) Å
V = 2014.4 (9) Å^3
Z = 4
D_x = 1.446 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 250 reflections
θ = 1.82–25.03°
μ = 0.117 mm^{-1}
T = 294 (1) K
Plate
0.28 × 0.26 × 0.14 mm
Colourless

Data collection

Enraf–Nonius diffractometer with FAST area detector
MADNES scans (Pflugrath & Messerschmidt, 1989)
Absorption correction: none
8231 measured reflections
2893 independent reflections

2076 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.098
$\theta_{\rm max}$ = 25.03°
$h = -8 \rightarrow 8$
$k = -19 \rightarrow 19$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.084
S = 0.837

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.323 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.256 e Å^{-3}
Extinction correction: none

2893 reflections
285 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C5a=C9a	1.358 (4)	C8=N9	1.286 (4)
N7—C8—N9—C9a	5.9 (5)	N5—C4a—C10a—N10	2.9 (4)
C4—C4a—C10a—O1	−2.7 (4)		

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

D—H· · ·*A*	*D*—H	H· · ·*A*	*D*· · ·*A*	*D*—H· · ·*A*
N7—H7· · ·O51$^{\rm i}$	0.86	2.219	2.886 (4)	134.3

Symmetry code: (i) $x - 1, y, z$.

Compound (4) crystallized in the orthorhombic system. Space group $P2_12_12_1$ was suggested by the systematic absences; it was assumed, and subsequently confirmed by the analysis. H atoms were treated as riding (C—H 0.93–0.98, N—H 0.86 Å). Non-methyl H atoms were located in difference maps, but examination of the area of the methyl H atoms using the *COFOUR* program in *NRCVAX* (Gabe *et al.*, 1989) indicated disorder. All H atoms were inserted into the atom list using positions calculated on the basis of the molecular geometry; the methyl H atoms were inserted as six half-H atoms.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992) and *FAST*/*MADNES* (Pflugrath & Messerschmidt, 1989). Cell refinement: *CAD*-4-*PC Software* and *FAST*/*MADNES*. Data reduction: *CAD*-4-*PC Software*, *FAST*/*MADNES* and *DATRD*2 (*NRCVAX*94; Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *NRCVAX*94 (Gabe *et al.*, 1989) and *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *PREP*8 (Ferguson, 1998).

We thank Professor M. Hursthouse of the EPSRC National X-ray Crystallography Service, UK, for the data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1253). Services for accessing these data are described at the back of the journal.

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Crystallographic evidence of the formation of an *N*-alkylated enammonium salt: 5-ethoxycarbonylmethyl-1-ethyl-2,3,6,7-tetrahydro-4*H*,12*H*-indolo[2,3-*a*]quinolizin-5-ium trifluoromethanesulfonate

Petra Bombicz and Alajos Kálmán

Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, H-1525 Budapest, POB 17, Hungary.
E-mail: akalman@cric.chemres.hu

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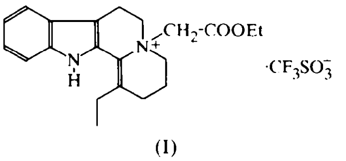
Abstract

The structure determination of the title compound, $C_{21}H_{27}N_2O_2^+ \cdot CF_3SO_3^-$, substantiates the possibility of a reaction in which the alkylation process of Wenkert enamines unexpectedly gives rise to an *N*-alkylated enammonium salt. The study of the molecular packing reveals that the small trifluoromethanesulfonate anions are located between the sheets of the cations, thus enjoying relatively high freedom of motion in their cavities.

Comment

The so-called Wenkert enamine is a widely used intermediate in the synthesis of vinca alkaloids (Szántay & Nemes, 1994). In the alkylation process of this Wenkert enamine, activated alkyl halides usually provide easier access to *C*-alkylated products as opposed to *N*-alkylated ones. However, with the use of ethoxycarbonylmethyl trifluoromethanesulfonate, an *N*-alkylated enammonium salt was unexpectedly obtained (Lukács *et al.*, 1996). The crystal structure determination of the title compound, (I), proves the inverted reactivity of C1 as opposed to the enamine. The exploitation of this *umpolung* (the inverted reactivity) is reported in detail by Lukács *et al.* (1998).



(I)

The molecular structure with displacement ellipsoids is depicted in Fig. 1. The molecule is built up from a planar indole and a puckered tetrahydro-4*H*,12*H*-quinolizine moiety. Deviations of atoms pertaining to the tetrahydro-4*H*,12*H*-quinolizine moiety from the best plane of the indole ring [given by the equation $-10.834(7)x + 4.891(8)y + -6.968(8)z = -14.814(3)$] are as follows: C1 = −0.282 (2), C2 = −0.268 (2), C3 = 0.203 (2), C4 = −0.311 (2), N5 = 0.243 (3), C6 = −0.481 (3), C7 = −0.011 (3) and C12b = −0.063 (3) Å. Ring *C* has a half-chair shape with puckering parameters of Q = 0.492 (2) Å, θ = 49.8 (2)°, φ = 35.0 (3)° (Cremer & Pople, 1975), whilst ring *D* is an envelope with C4 on the flap [Q = 0.501 (3) Å, θ = 129.6 (3)°, φ = 252.6 (3)°]. The quaternary ammonium base formed around N5 is characterized by a mean C—N bond length of 1.522 (9) Å and a mean tetrahedral bond angle of 109.5 (3)°. The atom S20$(2 - x, -y, 1 - z)$ is 5.267 (5) Å from the nearest N5 atom. The shortest distance between the positively charged N5 atom and one of the O atoms of the trifluoromethanesulfonate anion, O23$(\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z)$, is 4.006 (4) Å. The relatively small trifluoromethanesulfonate anions are located between the sheets of the cations (Fig. 2). Therefore, as shown by their large anisotropic displacement parameters, they have substantial freedom of motion in their cavities. The terminal ethyl group of the long ethoxy-

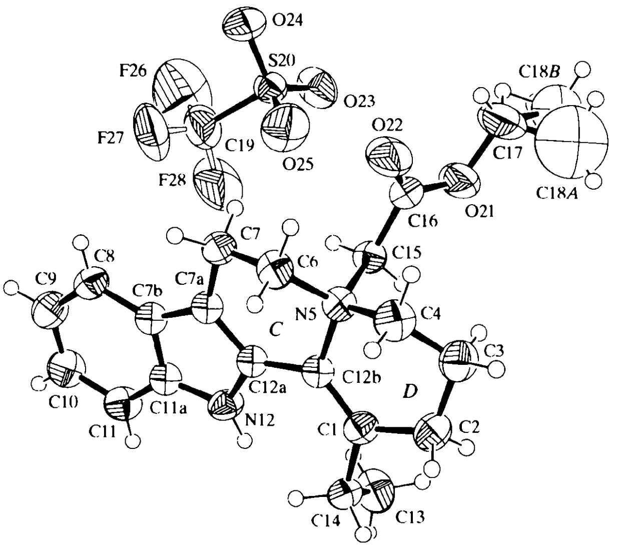


Fig. 1. *ORTEP* (Johnson, 1965) diagram of the compound showing atomic displacement parameters at the 50% probability level, atomic numbering and ring indicators. The two disordered positions of C18 are indicated.