a full-matrix least-squares routine (*SHELX76*; Sheldrick, 1976). All H atoms were located from the difference Fourier map and refined isotropically.

Support from the National Institute for General Medical Sciences (GM-21822) and the British Technology Group is gratefully acknowledged.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and stereoscopic views of all molecules have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71069 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1028]

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Acta Cryst. (1993). C**49**, 1649–1652

Structure of a 6-Tetrahydroxybutyl-Substituted 5,6,7,8-Tetrahydropteridine

Roy L. Beddoes, James R. Russell, C. David Garner and John A. Joule*

Chemistry Department, University of Manchester, Manchester M13 9PL, England

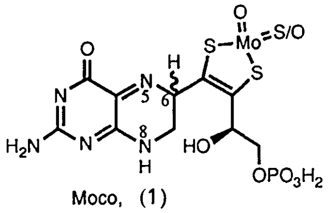
(*Received* 2 *September* 1992; *accepted* 11 *February* 1993)

Abstract

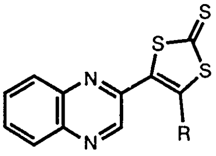
The crystal structure of 2-acetamido-5-benzyloxycarbonyl-3,4,5,6,7,8-hexahydro-4-oxo-6-(D-*arabino*-tetrahydroxybutyl)pteridine tetraacetate, (5), shows that reduction of 2-acetamido-3,4-dihydro-4-oxo-6-(D-*arabino*-tetrahydroxybutyl)pteridine tetraacetate, (4), with sodium cyanoborohydride in the presence of benzyl chloroformate achieves saturation of the pyrazine ring with regioselective protection at nitrogen N(5).

Comment

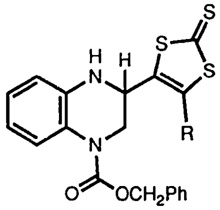
We are developing a synthetic route (Rowe, Garner, & Joule, 1985; Larsen, Garner & Joule, 1989; Larsen, Rowe, Garner & Joule, 1989; Russell, Garner & Joule, 1992*a*,*b*,*c*) to Moco (Rajagopalan, 1991; Johnson, 1980; Gardlik & Rajagopalan, 1990), (1), the cofactor of all molybdoenzymes except nitrogenase. The cofactor comprises a dihydropteridine carrying a functionalized side chain at C(6) on which are situated the S atoms which coordinate the metal centre. It is planned that the production of the requisite dihydropyrazine oxidation level, *cf.* (1), will involve (*a*) reduction of a precursor pteridine to the 5,6,7,8-tetrahydro level then (*b*) regioselective reoxidation to dihydro level, *i.e.* the introduction of unsaturation at N(5).



Moco, (1)



(2)

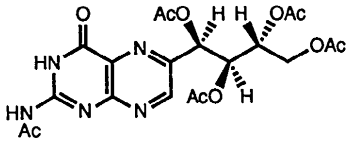


(3)

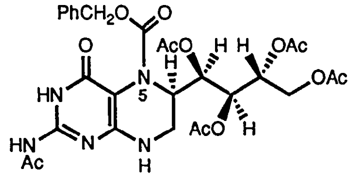
We have shown (Beddoes, Russell, Garner & Joule, 1993; Russell, Garner & Joule, 1992*a*,*b*) that reduction of quinoxalines of the general form (2) in the presence of benzyl chloroformate generates tetrahydroquinoxalines, (3), with the N atom which is remote from the substituent, protected as a urethane. In seeking to clarify both the stage at which the reduction should be carried out and also whether a comparable regiochemical preference would be found in a pteridine, we have reduced 2-acetamido-3,4-dihydro-4-oxo-6-(D-*arabino*-tetrahydroxybutyl)pteridine tetraacetate, (4), with sodium cyanoborohydride in the presence of benzyl chloroformate in methanol. A mixture of diastereoisomers was formed, recrystallization of which produced material

Acta Crystallographica Section C
ISSN 0108-2701 ©1993

shown to have structure (5), by X-ray crystallographic examination. This shows that a different regioselectivity pertains in this reduction/protection, in that in the pteridine series the urethane group is *adjacent* to the pyrazine ring substituent.

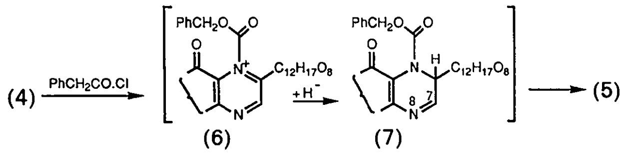


(4)

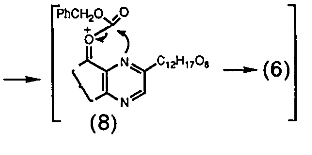


(5)

The production of (5), with the added urethane located at what is clearly the more hindered of the two pyrazine N atoms, and in contrast to the results obtained with quinoxalines, demands explanation; there seem to be two possible rationalizations. We suggest that there may be sufficiently greater basicity/nucleophilicity at N(5), than at N(8), influenced as it is by electron-withdrawal by the *A*-ring carbonyl, to overcome the steric discouragement, *i.e.* that (6) is formed faster than the equivalent N(8)-acylated pyrazinium, and that (6) is then reduced to (7), followed rapidly by reduction of the residual 7,8-imine double bond in (7).



An alternative explanation is that the N-5-acylation may be achieved *via* an intramolecular delivery [arrows on (8)] from an initial *O*-acylated intermediate, (8).



The atomic parameters for the non-H atoms of 2-acetamido-5-benzyloxycarbonyl-3,4,5,6,7,8-hexahydro-4-oxo-6-(D-*arabino*-tetrahydroxybutyl)pteridine tetraacetate are listed in Table 1; Table 2 lists selected bond lengths and bond angles; Fig. 1 shows a *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule and the numbering system used in the tables.

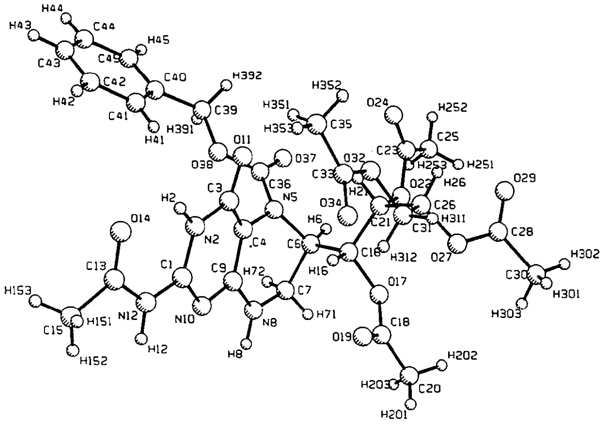


Fig. 1. A *PLUTO* drawing of compound (5) showing the numbering scheme.

The reduced pyrazine ring adopts a flattened-boat conformation. It is noteworthy that the urethane N atom N(5) is substantially pyramidalized, with the sum of angles being 355.8°. Two intermolecular hydrogen bonds (N8—H···O14 and N12—H···O11) are a consequence of a twofold screw axis situated at $(\frac{1}{2},y,\frac{1}{2})$.

Experimental

Crystal data

$C_{28}H_{33}N_5O_{12}$
$M_r = 631.59$
Monoclinic
$P2_1$
$a = 11.268\ (2)$ Å
$b = 11.996\ (1)$ Å
$c = 12.297\ (1)$ Å
$\beta = 102.204\ (9)°$
$V = 1624.6\ (3)$ Å^3
$Z = 2$
$D_x = 1.291$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 23 reflections
$\theta = 31.16$–$39.8°$
$\mu = 0.828$ mm^{-1}
$T = 296\ (1)$ K
Prismatic
0.450 × 0.110 × 0.060 mm
Colourless

Data collection

Rigaku AFC-5R diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*, Walker & Stuart, 1983)
$T_{\min} = 0.40$, $T_{\max} = 1.36$
2706 measured reflections
2562 independent reflections
2164 observed reflections [$I>3.0\sigma(I)$]

$R_{\rm int} = 0.017$
$\theta_{\max} = 60°$
$h = -11 \rightarrow 12$
$k = -11 \rightarrow 13$
$l = -13 \rightarrow 12$
3 standard reflections monitored every 150 reflections intensity variation: −0.4%

Refinement

Refinement on *F*
Final $R = 0.058$
$wR = 0.071$
$S = 2.48$
2164 reflections
405 parameters
H-atom parameters not refined

$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974); Ibers & Hamilton (1964)

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

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$B_{\rm eq}$
C1	0.5052 (6)	0.25	0.5018 (5)	3.3 (2)
N2	0.4860 (5)	0.3582 (6)	0.5222 (4)	3.5 (2)
C3	0.4694 (6)	0.3954 (7)	0.6258 (5)	3.1 (2)
C4	0.4867 (6)	0.3123 (7)	0.7080 (5)	3.1 (3)
N5	0.4754 (5)	0.3357 (6)	0.8178 (4)	3.2 (2)
C6	0.4076 (6)	0.2511 (7)	0.8659 (5)	3.5 (3)
C7	0.4714 (7)	0.1388 (7)	0.8603 (5)	4.0 (3)
N8	0.4860 (6)	0.1188 (6)	0.7482 (4)	4.0 (2)
C9	0.4938 (6)	0.2014 (7)	0.6776 (5)	3.4 (3)
N10	0.5045 (5)	0.1700 (6)	0.5736 (4)	3.3 (2)
O11	0.4432 (5)	0.4937 (6)	0.6373 (4)	4.1 (2)
N12	0.5252 (5)	0.2189 (6)	0.3998 (4)	3.8 (2)
C13	0.5401 (8)	0.2866 (7)	0.3151 (6)	4.6 (3)
O14	0.5247 (6)	0.3873 (6)	0.3180 (4)	6.1 (3)
C15	0.574 (1)	0.2289 (8)	0.2178 (6)	7.2 (5)
C16	0.2758 (7)	0.2570 (7)	0.8059 (5)	3.9 (3)
O17	0.2143 (5)	0.1594 (6)	0.8353 (4)	4.4 (2)
C18	0.161 (1)	0.0918 (8)	0.7512 (8)	6.3 (4)
O19	0.1546 (8)	0.1131 (7)	0.6548 (7)	9.3 (4)
C20	0.112 (1)	−0.011 (1)	0.7931 (8)	9.0 (6)
C21	0.2162 (7)	0.3622 (7)	0.8360 (5)	4.0 (3)
O22	0.2259 (5)	0.3587 (6)	0.9548 (4)	4.9 (2)
C23	0.2441 (8)	0.456 (1)	1.0110 (7)	6.1 (4)
O24	0.2542 (7)	0.5437 (7)	0.9657 (6)	7.7 (4)
C25	0.250 (1)	0.436 (1)	1.1311 (8)	8.8 (6)
C26	0.0842 (7)	0.3863 (8)	0.7808 (7)	5.2 (3)
O27	0.0042 (7)	0.3006 (7)	0.8011 (6)	6.9 (3)
C28	−0.055 (1)	0.315 (1)	0.881 (1)	8.4 (7)
O29	−0.0361 (7)	0.3938 (9)	0.9474 (6)	8.7 (4)
C30	−0.150 (1)	0.228 (1)	0.880 (1)	13 (1)
C31	0.0610 (9)	0.391 (1)	0.6547 (8)	6.7 (4)
O32	0.1227 (6)	0.4883 (8)	0.6230 (5)	7.4 (3)
C33	0.127 (1)	0.501 (1)	0.516 (1)	9.1 (7)
O34	0.080 (2)	0.429 (1)	0.4520 (7)	18.6 (9)
C35	0.176 (1)	0.607 (1)	0.492 (1)	11.0 (8)
C36	0.5547 (6)	0.4045 (7)	0.8876 (5)	3.6 (3)
O37	0.5538 (5)	0.4182 (6)	0.9852 (3)	5.0 (2)
O38	0.6294 (4)	0.4550 (6)	0.8338 (3)	4.2 (2)
C39	0.7102 (7)	0.5364 (8)	0.8953 (6)	5.1 (3)
C40	0.7823 (8)	0.5890 (8)	0.8197 (7)	5.2 (4)
C41	0.755 (1)	0.580 (1)	0.7076 (8)	8.6 (6)
C42	0.821 (1)	0.632 (2)	0.639 (1)	11.5 (9)
C43	0.918 (1)	0.692 (1)	0.685 (1)	10.5 (8)
C44	0.951 (1)	0.701 (1)	0.801 (2)	11.9 (9)
C45	0.882 (1)	0.651 (1)	0.867 (1)	8.8 (6)

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

C1—N2	1.348 (7)	C7—N8	1.443 (7)
C1—N10	1.306 (7)	N8—C9	1.333 (8)
C1—N12	1.371 (8)	C9—N10	1.362 (7)
N2—C3	1.400 (7)	N12—C13	1.359 (8)
C3—C4	1.403 (8)	C13—O14	1.222 (7)
C3—O11	1.231 (7)	C16—O17	1.445 (7)
C4—N5	1.411 (7)	C16—C21	1.513 (9)
C4—C9	1.390 (8)	C21—O22	1.442 (8)
N5—C6	1.468 (8)	C21—C26	1.53 (1)
N5—C36	1.375 (8)	C26—O27	1.423 (9)
C6—C7	1.535 (9)	C26—C31	1.52 (1)
C6—C16	1.514 (9)	C31—O32	1.45 (1)
N2—C1—N10	123.9 (6)	O17—C16—C21	110.7 (5)
N2—C1—N12	119.7 (5)	C16—O17—C18	116.9 (5)
N10—C1—N12	116.4 (5)	O17—C18—O19	123.6 (7)
C1—N2—C3	122.3 (5)	O17—C18—C20	111.7 (7)
N2—C3—C4	113.9 (5)	O19—C18—C20	124.7 (8)
N2—C3—O11	119.4 (5)	C16—C21—O22	106.3 (5)
C4—C3—O11	126.7 (6)	C16—C21—C26	119.4 (6)
C3—C4—N5	121.4 (5)	O22—C21—C26	108.3 (5)
C3—C4—C9	119.5 (5)	C21—O22—C23	117.8 (6)
N5—C4—C9	118.1 (5)	O22—C23—O24	122.5 (8)
C4—N5—C6	114.0 (5)	O22—C23—C25	110.2 (9)
C4—N5—C36	122.5 (5)	O24—C23—C25	127.3 (9)
C6—N5—C36	119.3 (5)	C21—C26—O27	112.2 (6)
N5—C6—C7	107.5 (5)	C21—C26—C31	113.7 (7)
N5—C6—C16	108.2 (5)	O27—C26—C31	103.1 (7)
C7—C6—C16	116.1 (6)	C26—O27—C28	118.3 (8)
C6—C7—N8	109.8 (5)	O27—C28—O29	124 (1)
C7—N8—C9	122.4 (5)	O27—C28—C30	112 (1)
C4—C9—N8	121.4 (5)	O29—C28—C30	124 (1)
C4—C9—N10	122.6 (5)	C26—C31—O32	108.3 (7)
N8—C9—N10	115.9 (5)	C31—O32—C33	118.4 (9)
C1—N10—C9	116.5 (5)	O32—C33—O34	117 (1)
C1—N12—C13	127.5 (5)	O32—C33—C35	114 (1)
N12—C13—O14	121.8 (6)	O34—C33—C35	129 (1)
N12—C13—C15	115.4 (6)	N5—C36—O37	123.9 (6)
O14—C13—C15	122.8 (6)	N5—C36—O38	111.2 (5)
C6—C16—O17	108.3 (5)	O37—C36—O38	124.9 (6)
C6—C16—C21	111.2 (5)		

Synthesized by reduction of compound (4) with sodium cyanoborohydride in the presence of benzyl chloroformate and recrystallization from 95% aqueous ethanol. Computer programs used: *SHELX*86 (Sheldrick, 1985); *TEXSAN* (Molecular Structure Corporation, 1985); *PLUTO* (Motherwell & Clegg, 1978).

We thank the SERC, UK, for a research fellowship (JRR) and for funds for the purchase of the Rigaku AFC-5R diffractometer.

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 71090 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1028]

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Acta Cryst. (1993). C**49**, 1652–1654

Tetra(*n*-butyl)ammonium Trifluoromethanesulfonate

ALEXANDER J. BLAKE,* CHRISTIAN RADEK AND MARTIN SCHRÖDER

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

(*Received* 21 *October* 1992; *accepted* 10 *February* 1993)

Abstract

The title structure comprises two ion pairs in each asymmetric unit. There are no close contacts between any of the ions. Although the structure determination was carried out at reduced temperature there are large vibration amplitudes for some F atoms and disorder in one of the *n*-butyl chains.

Comment

Trifluoromethanesulfonic acid has been reported in its anhydrous form (Bartmann & Mootz, 1990) and with increasing degrees of hydration (Lundgren & Spencer, 1973; Delaplane, Lundgren & Olovsson, 1975*a*,*b*; Lundgren, 1978*a*,*b*). One series of salts with nonaaqualanthanide(III) cations has been reported (Harrowfield, Kepert, Patrick & White, 1983; Castellano, Machado, Santos & Vicentini, 1985; Chatterjee, Maslen & Watson, 1988). Salts with the cations $[V(H_2O)_6]^{2+}$ (Holt, Larkworthy, Leigh, Povey & Smith, 1989) and $[V(H_2O)_6]^{3+}$ (Cotton, Fair, Lewis, Mott, Ross, Schultz & Williams, 1984) are also known. Although $CF_3SO_3^-$ is a common counteranion for complex metal ions, there are relatively few examples with simple inorganic cations such as oxonium (Lundgren, Olovsson & Tellgren, 1978), ammonium (Brauer & Ganswein, 1975) and seleninyl (Kapoor, Kapoor, Sawyer & Wadhawan, 1988). Salts containing simple alkylammonium cations are even rarer (*e.g.* $CH_3NH_3^+$; Alberts, Noltes, Roelofsen & Spek, 1982).

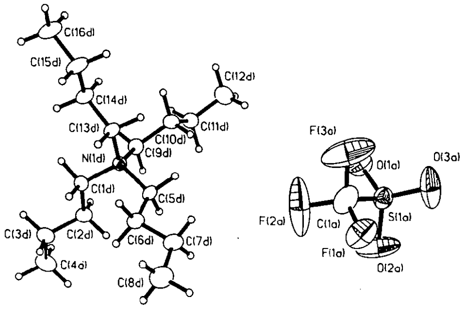

Fig. 1. View of one ion pair showing the labelling of the non-H atoms. Thermal ellipsoids are drawn at the 50% probability level except for H atoms which have artificial radii of 0.10 Å^2 for clarity.

Selected geometric parameters are shown in Table 1. C—C bond lengths are normal; bond angles are in the range 108–112° except for those listed; torsion angles are all in the range 60 ± 10° or 180 ± 10° except those listed.

Experimental

Crystal data

$C_{16}H_{36}N^+.CF_3SO_3^-$
$M_r = 391.5$
Monoclinic
$P2_1/a$
$a = 15.531\ (4)$ Å
$b = 18.136\ (6)$ Å
$c = 16.895\ (4)$ Å
$\beta = 114.674\ (20)°$
$V = 4324$ Å^3
$Z = 8$
$D_x = 1.202$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 41 reflections
$\theta = 15$-$16°$
$\mu = 0.181$ mm^{-1}
$T = 150.0$ K
Block
1.04 × 0.70 × 0.70 mm
Colourless
Crystal source: recrystallization from MeOH/H$_2$O

Data collection

Stoe Stadi-4 diffractometer
ω-2θ scans
Absorption correction: none
5901 measured reflections
5901 independent reflections
3823 observed reflections $[F>4\sigma(F)]$
$\theta_{\max} = 22.5°$
$h = -16 \rightarrow 15$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 18$
3 standard reflections frequency: 60 min intensity variation: 2.5% (isotropic decay)

Acta Crystallographica Section C
ISSN 0108-2701 ©1993