Triclinic
$P\overline{1}$
a = 6.685 (2) Å
b = 13.2357 (11) Å
c = 14.8763 (19) Å
α = 93.677 (9)°
β = 98.114 (16)°
γ = 90.359 (14)°
V = 1300.3 (5) Å^3
Z = 4
D_x = 1.412 Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
θ = 1.54–24.97°
μ = 0.103 mm^{-1}
T = 293 (2) K
Plate
0.64 × 0.44 × 0.16 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
4562 measured reflections
4562 independent reflections
2806 reflections with $I > 2\sigma(I)$

θ_{max} = 24.97°
$h = 0 \rightarrow 7$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.148
S = 0.998
2806 reflections
302 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.061P)^2 + 0.9105P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.468 e Å^{-3}
$\Delta\rho_{min}$ = −0.253 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0070 (16)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C1—N1	1.350 (3)	C14—N5	1.426 (3)
C4—N4	1.425 (3)	C17—N8	1.354 (3)
C1—N1—C7	123.2 (2)	C17—N8—C26	123.4 (2)
C1—N1—C13	120.0 (2)	C17—N8—C20	119.5 (2)
C7—N1—C13	116.5 (2)	C26—N8—C20	116.5 (2)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Xtal3.5* (Hall *et al.*, 1995). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEX* (McArdle, 1995). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1090). Services for accessing these data are described at the back of the journal.

References

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius. Delft. The Netherlands.
Hall, S. R., Flack, H. D. & Stewart, J. M. (1995). Editors. *Xtal3.5 Reference Manual*. Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
Õki, M. (1985). *Application of Dynamic NMR Spectroscopy to Organic Chemistry*, p. 315. Florida: VCH Publishers, Inc.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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A 1-alkylated pteridine, $C_{15}H_{19}ClN_6O_3$

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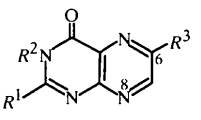
Abstract

The crystal structure of 6-chloro-2-(*N*,*N*-dimethylaminomethyleneamino)-1-(pivaloyloxymethyl)pteridin-4-one confirms that the reaction of pterin 8-oxide with acetyl chloride in trifluoroacetic acid produces the 6-chloride, and that the minor product from alkylation of 6-chloro-2-(*N*,*N*-dimethylaminomethyleneamino)pteridin-4-one with chloromethyl pivaloate in dimethylformamide with potassium carbonate, is N-1-alkylated and not N-8- or C-4-O-alkylated.

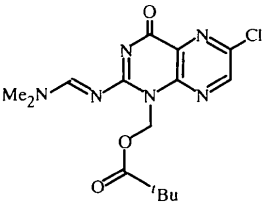
Comment

The regioselective N-8-oxidation (Yamamoto *et al.*, 1973) of pterin (2-aminopteridin-4-one), (1*a*), and the conversion (Taylor & Kobylecki, 1978) of this *N*-oxide into 6-chloropterin, (1*b*), with a combination of acetyl chloride and trifluoroacetic acid, is a useful route to a pteridine functionalized on the pyrazine ring, albeit that the regiochemistry of this last transformation is not at all what would have been expected by analogy with other azine *N*-oxide chemistry. No X-ray crystallographic evidence has been advanced for the regiochemical outcome of this transformation.



(1)

	R^1	R^2	R^3
(1*a*)	H_2N	H	H
(1*b*)	H_2N	H	Cl
(1*c*)	$Me_2NCH{=}N$	H	Cl
(1*d*)	$Me_2NCH{=}N$	$^tBu\,CO_2CH_2$	Cl



(2)

In our studies related to the cofactor of the oxomolybdoenzymes (for a summary see Collison *et al.*, 1996; for more recent work see Dinsmore *et al.*, 1997, 1998; Greatbanks *et al.*, 1997; Davies *et al.*, 1997; Bradshaw *et al.*, 1998), which comprises a special pterin carrying a side-chain at C-6, we envisaged using (1*b*) as a synthetic intermediate, provided it could be satisfactorily verified that the introduced chlorine is indeed located at C-6, and not at C-7, which would have been expected by analogy with the chemistry of simpler azine *N*-oxides. Masking the amino group in (1*b*) by reaction with Brederick's reagent, giving (1*c*), then reaction with chloromethyl pivaloate in the presence of potassium carbonate and sodium iodide, gave (1*d*) for our synthetic studies, and a second alkylated product. In principle, the anion produced from (1*c*) could react at N-3 [giving (1*d*)], at the C-4 O atom, at N-1 or at N-8. It was to determine the site of alkylation in this second product, and at the same time to confirm the position of the halogen in each of these molecules, that the present X-ray crystal structure determination was carried out.

Exclusive N-3-alkylation for base-catalysed alkylation of 2,3-dimethylpterin, using acrylonitrile as the alkylating agent (Angier & Curran, 1959), and exclusive N-8-methylation of pterin itself (Brown & Jacobsen, 1961) have been reported. It has been observed that a much larger proportion of N-8-methylation occurs when the reaction with iodomethane is carried out in neutral solution (Armarego & Milloy, 1977). The formation of mixtures of N-1- and N-3-methylated products from base-catalysed reactions of 6,7-dimethylpterin (Angier & Curran, 1961), 6,7-diphenylpterin (Angier, 1963), pterin-6-carboxylic acid (Angier & Curran, 1962), and 6-methylpterin (Armarego & Milloy, 1977) have been reported, but no crystallographic support was provided for the structural assignments of any of the N-1-methylated products. The crystal structure (Fig. 1) of the minor alkylation product from (1*c*) shows it to be the N-1-alkylated pterin, (2).

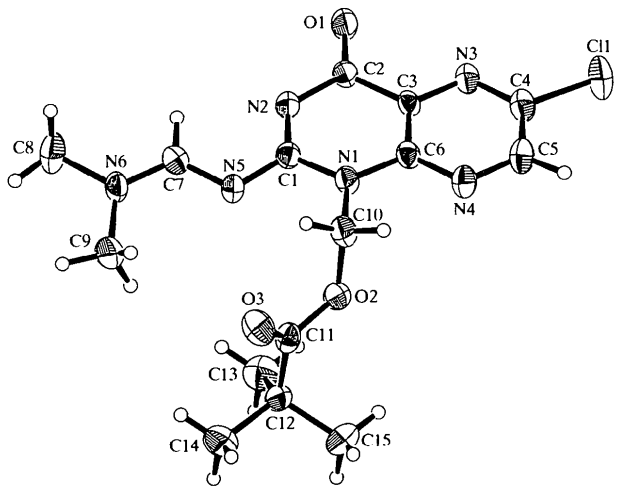


Fig. 1. *ORTEP* (Johnson, 1965) plot of the molecule of (2), showing the atom-numbering scheme of the non-H atoms. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

The reaction of 6-chloro-2-(*N*,*N*-dimethylaminomethyleneamino)pteridin-4-one with chloromethyl pivaloate, in the presence of potassium carbonate as base, gave 6-chloro-2-(*N*,*N*-dimethylaminomethyleneamino)-3-(pivaloyloxymethyl)-pteridin-4-one, (1*d*), and 6-chloro-2-(*N*,*N*-dimethylaminomethyleneamino)-1-(pivaloyloxymethyl)pteridin-4-one, (2), in a ratio of *ca* 1.3:1. Separation of the isomers and crystallization of the minor component from ethyl acetate gave material suitable for X-ray crystal examination (m.p. 492–494 K).

Crystal data

$C_{15}H_{19}ClN_6O_3$
M_r = 366.81
Monoclinic
$P2_1/n$
a = 11.7770 (11) Å
b = 9.3742 (5) Å
c = 17.0675 (15) Å
β = 106.623 (7)°
V = 1805.5 (3) Å^3
Z = 4
D_x = 1.349 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 14.4–17.0°
μ = 2.122 mm^{-1}
T = 296 (2) K
Tabular
0.35 × 0.17 × 0.10 mm
Orange

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North *et al.*, 1968)
T_{min} = 0.637, T_{max} = 0.809
3883 measured reflections
3697 independent reflections

2168 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 79.45°
$h = -11 \rightarrow 15$
$k = -10 \rightarrow 11$
$l = -20 \rightarrow 21$
3 standard reflections every 150 reflections
intensity decay: 1.73%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.167
S = 1.073

$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 1.562P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004

3697 reflections
231 parameters
H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{max}$ = 0.204 e Å^{-3}
$\Delta\rho_{min}$ = −0.183 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1002). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, M., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Angier, R. B. (1963). *J. Org. Chem.* **28**, 1509–1513.
Angier, R. B. & Curran, W. V. (1959). *J. Am. Chem. Soc.* **81**, 5650–5655.
Angier, R. B. & Curran, W. V. (1961). *J. Org. Chem.* **26**, 2129–2132.
Angier, R. B. & Curran, W. V. (1962). *J. Org. Chem.* **27**, 892–898.
Armarego, W. L. F. & Milloy, B. A. (1977). *Aust. J. Chem.* **30**, 2023–2028.
Bradshaw, B., Dinsmore, A., Garner, C. D. & Joule, J. A. (1998). *Chem. Commun.* pp. 417–418.
Brown, D. J. & Jacobsen, N. W. (1961). *J. Chem. Soc.* pp. 4413–4420.
Collison, D., Garner, C. D. & Joule, J. A. (1996). *Chem. Soc. Rev.* pp. 25–32.
Davies, E. S., Beddoes, R. L., Collison, D., Dinsmore, A., Docrat, A., Joule, J. A., Wilson, C. R. & Garner, C. D. (1997). *J. Chem. Soc. Dalton Trans.* pp. 3985–3996.
Dinsmore, A., Birks, J. H., Garner, C. D. & Joule, J. A. (1997). *J. Chem. Soc. Perkin Trans.* 1, pp. 801–807.
Dinsmore, A., Garner, C. D. & Joule, J. A. (1998). *Tetrahedron*, **54**, 3291–3302.
Greatbanks, S. P., Hillier, I. H., Garner, C. D. & Joule, J. A. (1997). *J. Chem. Soc. Perkin Trans.* 2, pp. 1529–1534.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1989). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-2. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Taylor, E. C. & Kobylecki, R. (1978). *J. Org. Chem.* **43**, 680–683.
Yamamoto, H., Hutzenlaub, W. & Pfleiderer, W. (1973). *Chem. Ber.* **106**, 3175–3193.

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N-(*p*-Chlorobenzoyl)-*N*-methylaniline

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Abstract

The crystal and molecular structure of the title compound [alternative name: *p*-chlorophenyl (*N*-methylanilino)methyl ketone], $C_{15}H_{14}ClNO$, has been determined by X-ray crystallography. There are two independent molecules in the asymmetric unit. The packing shows that it is unlikely for there to be intermolecular charge transfer in the crystal.

Comment

As some indoles are of pharmacological interest as potential neuro-active drugs, a method of synthesizing 3- and 2-functionalized derivatives was required (Smith & Visnick, 1985; Walkup & Linder, 1985). An alternative methodology uses phenacylanilines as starting products (Brown & Mann, 1948): we used *N*-methyl-*p*-chlorophenacylaniline which transforms to 1-methyl-3- or 2-*p*-chlorophenylindole or a mixture of both under different acid catalysts (Rodríguez & Martín-Villamil, 1997, unpublished results). The molecular structure of the phenacyl precursor was determined to investigate the catalytic reaction behaviour and to look into possible charge–transfer complexation (Abdulla *et al.*, 1985).

The structure of the title compound, (I), consists essentially of planar and almost perpendicular *N*-methylaniline and *p*-chlorobenzoyl fragments, linked through a methylene bridge between the aniline-N and the carbonyl-C atoms. There are two independent molecules in the asymmetric unit (Fig. 1). The two molecules differ slightly in their torsion and dihedral angles. The dihedral angles between the C2–C7 and C12–C17 rings are 76.05 (1) for molecule *A* and 86.43 (1)° for molecule *B*. The torsion angle C5—C8—C10—N11 is −179.0 (2) in *A* and −162.4 (2)° in *B*. The chloro substituent is essentially coplanar with the ring to which it is attached in both molecules. Significant intermolecular interactions occur between the phenyl rings; the crystal packing involves T-shaped contacts between the aniline