Table 1. *Selected geometric parameters (Å, °) for (I) and (II)*

	(I)	(II)
C1—C8a	1.571 (4)	1.587 (2)
C1—C15	1.477 (5)	1.538 (2)
C1—C16	1.482 (4)	1.474 (2)
C2—C9	1.458 (4)	1.467 (2)
C1—C2	1.545 (4)	1.540 (2)
C2—C3	1.349 (4)	1.340 (2)
C3—C3a	1.432 (4)	1.433 (2)
C4—C3a	1.344 (4)	1.345 (2)
C4—C5	1.439 (5)	1.438 (2)
C5—C6	1.338 (5)	1.345 (3)
C6—C7	1.441 (5)	1.434 (3)
C7—C8	1.338 (5)	1.342 (2)
C8—C8a	1.497 (4)	1.505 (2)
C8a—C3a	1.506 (4)	1.514 (2)
C2—C1—C8a	104.3 (2)	103.8 (1)
C1—C2—C3	108.5 (3)	109.7 (1)
C2—C3—C3a	113.4 (3)	113.3 (1)
C3—C3a—C8a	108.7 (2)	108.8 (1)
C4—C3a—C8a	122.1 (3)	123.8 (2)
C3a—C4—C5	124.4 (3)	124.9 (2)
C4—C5—C6	125.7 (4)	125.6 (2)
C5—C6—C7	125.9 (4)	125.9 (2)
C6—C7—C8	125.4 (4)	127.4 (2)
C7—C8—C8a	120.7 (3)	121.3 (2)
C8—C8a—C3a	107.9 (2)	107.8 (1)
C1—C8a—C3a	103.4 (2)	103.3 (1)

Table 2. *Comparison of cycloheptatriene conformation*

REFCODE†	α (°)‡	β (°)‡	C3a—C8a (Å)	Reference
System (III)				
DMDPCH	52.6	34.3	2.410 (7)	Stegemann & Lindner (1979)
HEHWIA	48.8	28.1	2.387 (4)	Burnett *et al.* (1994)
System (IV)				
(I)	53.5 (3)	27.3 (2)	2.428 (4)	Present work
(II)	50.9 (2)	25.16 (9)	2.439 (2)	Present work
CRCAAZ	50.4	6.6	2.39 (5)	
	58.5	9.5	2.39 (5)	Brown *et al.* (1966)
HPHAZO	47.2	24.5	2.453 (8)	Van de Grampel *et al.* (1971)
FAPMOY	53.1	26.4	2.417 (6)	Daub *et al.* (1986)
DELCUS	53.3	27.6	2.436 (4)	Daub *et al.* (1985)
System (V)				
BETBEH	8.2	0.9	2.499 (2)	Reichardt *et al.* (1985)
HEPFUL	24.7	15.7	2.492 (5)	Thomas & Coppens (1972)
MCHFUL	45.3	20.1	2.474 (7)	Shimanouchi *et al.* (1974)
TAFFAH	36.6	28.9	2.461 (4)	Badejo *et al.* (1990)

† The refcodes are those used by Cambridge Structural Database (Allen & Kennard, 1993). ‡ S.u. values for α and β angles are not given in the original articles.

Data collection: *PW*1100/20 *Software* (Phillips, 1973) for (I); *Rigaku MSC/AFC Software* (Rigaku Corporation, 1988) for (II). Cell refinement: *PW*1100/20 *Software* for (I); *Rigaku MSC/AFC Software* for (II). Data reduction: *PROCN* in *PW*1100/20 *Software* for (I); *Rigaku MSC/AFC Software* for (II). For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976) and *TEXSAN* (Molecular Structure Corporation, 1993); software used to prepare material for publication: WORD6.0.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1031). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1667–1669

N-3-Allylation of 2-(*N*,*N*-Dimethylaminomethyleneamino)-6-formylpteridin-4-one

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Abstract

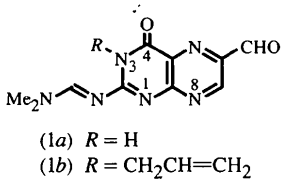
The reaction of 2-(*N*,*N*-dimethylaminomethyleneamino)-6-formylpteridin-4-one with allyl bromide in the presence of diazabicycloundecane as base leads

to allylation on N3 and the production of the title compound, 3-allyl-2-(*N*,*N*-dimethylaminomethyleneamino)-6-formylpteridin-4-one, $C_{13}H_{14}N_6O_2$.

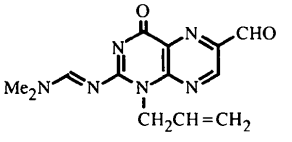
Comment

Recently, X-ray structure determinations of aldehyde oxidase from *Desulfovibrio gigas* (Romão *et al.*, 1995), DMSO reductase from *Rhodobacter sphaeroides* (Schindelin, Kisker, Hilton, Rajagopalan & Rees, 1996), and of the tungstopterin enzyme ferredoxin aldehyde oxidoreductase from *Pyrococcus furiosus* (Chan, Mukund, Kletzin, Adams & Rees, 1995) have clarified earlier suggestions based on degradative work (Johnson, Wuebbens & Rajagopalan, 1989, and references therein) for the structure of Moco, the ubiquitous cofactor of the oxomolybdoenzymes.

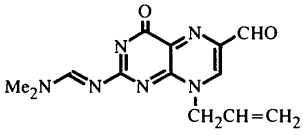
In our studies (for a summary see Collison, Garner & Joule, 1996) aimed both at clarifying the mode of action of Moco *via* the synthesis and study of model compounds, and also in our work towards a total synthesis of the cofactor, we required means for the selective protection of the pyrimidine ring of pteridine intermediates, thereby also improving organic solvent solubility. In several cases (Dinsmore, Birks, Garner & Joule, 1997), we showed that the two nitrogen H atoms of the 2-amino substituent can be masked by reaction with bis(dimethylamino)-*tert*-butoxymethane (Bredereck's reagent) in DMF at 333 K generating compounds such as (1*a*). It remained to block off the N3 H atom, certainly an important contributor to the sparing solubility.



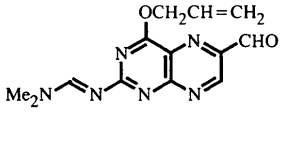
(1*a*) R = H
(1*b*) R = $CH_2CH{=}CH_2$



(2)



(3)



(4)

Reaction of the anion, produced by removing a proton from N3 in (1*a*), with an electrophilic alkylating agent could take place in principle at N1, N3, N8 or at the O atom at position 4, which would generate (where the alkylating agent is allyl bromide) (2), (1*b*) (the title compound), (3) or (4), respectively. The formation of mixtures of N1- and N3-methylated (Armarego & Milloy, 1977) and of N8-methylated (Brown & Jacobsen, 1961) pteridines has been reported in similar but simpler situations. In the case of (1*a*), there is a large substituent at the 2-position and we considered that this might have the effect of discouraging attack at the adjacent N atoms and encouraging attack at the less hindered N8 or 4-O-atom positions. It was in order to establish unambiguously the position of the introduced allyl group that we undertook this X-ray crystal structure determination.

The analysis showed the allylation product to have structure (1*b*), with the introduced allyl group at N3. Spectroscopic comparisons then allowed analogous assignments to be made to the methylation, methoxyethoxymethylation and benzylation products from (1*a*) (Dinsmore *et al.*, 1997).

The X-ray structure shows a planar pteridine ring system with the *N*,*N*-dimethylaminomethyleneamino unit twisted slightly (about 9.7°) out of this plane, no doubt to minimize interaction with the adjacent allyl substituent. The latter also orients to minimize interactions: the torsion angles C2—N3—C31—C32 [−85.8 (3)°] and C4—N3—C31—C32 [95.4 (3)°] being close to 90° and the vinyl group avoiding the N3 substituent by orienting with a torsion angle −116.8 (4)° for N3—C31—C32—C33. As is to be expected, adverse electronic interaction between the polarized aldehyde carbonyl and the similarly polarized ring C=N unit to which it is attached is minimized by the orientation of the former, maximizing the distance between N and O atoms.

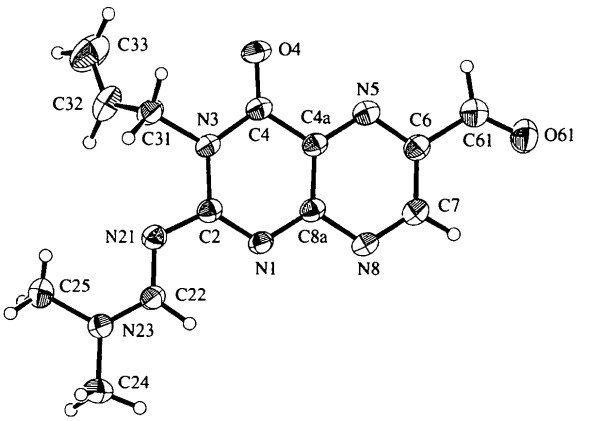


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule of (1*b*) with ellipsoids at the 30% probability level and H atoms shown as small circles of arbitrary radii.

Experimental

Allylation of (1*a*) was carried out as described (Dinsmore *et al.*, 1997) and a sample for X-ray analysis crystallized from ethyl acetate (m.p. 466–470 K).

Crystal data

$C_{13}H_{14}N_6O_2$
M_r = 286.30
Mo $K\alpha$ radiation
λ = 0.71069 Å

Monoclinic	Cell parameters from 16 reflections
$P2_1/n$	θ = 10.9–18.8°
a = 11.056 (4) Å	μ = 0.098 mm^{-1}
b = 8.340 (2) Å	T = 296 K
c = 15.5461 (12) Å	Block
β = 104.829 (13)°	0.37 × 0.35 × 0.20 mm
V = 1385.6 (6) Å^3	Amber
Z = 4	
D_x = 1.372 Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-5*R* diffractometer	1771 reflections with $I > 2\sigma(I)$
ω–2θ scans	R_{int} = 0.011
Absorption correction:	θ_{max} = 25.06°
ψ scans (North, Phillips & Mathews, 1968)	h = 0 → 13
T_{min} = 0.947, T_{max} = 1.000	k = 0 → 9
2575 measured reflections	l = −18 → 17
2442 independent reflections	3 standard reflections
	every 150 reflections
	intensity variation: 1.5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.069P)^2 + 0.476P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.050	$(\Delta/\sigma)_{max}$ = 0.002
$wR(F^2)$ = 0.147	$\Delta\rho_{max}$ = 0.33 e Å^{-3}
S = 1.045	$\Delta\rho_{min}$ = −0.18 e Å^{-3}
2441 reflections	Extinction correction: none
244 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
H atoms treated by a mixture of constrained and independent refinement	

The structure was solved by direct methods (*SIR*92; Altomare *et al.*, 1994) and expanded using Fourier techniques (*DIRDIF*94; Beurskens *et al.*, 1994). H atoms were found by difference Fourier techniques. Some were refined isotropically and, for the the remainder, coordinates were refined and the isotropic displacement parameters were fixed.

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 refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN*. 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: BM1143). Services for accessing these data are described at the back of the journal.

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Polysulfonylamines. LXXXIX.† *N*,*N*-Bis(methylsulfonyl)benzylamine

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Abstract

The two independent molecules of the title compound, $C_9H_{13}NO_4S_2$, are inverted with respect to each other but otherwise closely similar; unusually, a racemate thus crystallizes in a chiral space group ($P2_12_12_1$ with Z = 8). As is normal for compounds of type *R*—$N(SO_2CH_3)_2$, the C—N bonds [both 1.493 (3) Å] are lengthened with respect to standard values for acyclic

† Part LXXXVIII: Lange, Moers, Blaschette & Jones (1997).