1474 measured reflections	3 standard reflections
1466 independent reflections	every 200 reflections
1168 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$\Delta\rho_{max} = 0.193$ e Å^{-3}
$wR(F^2) = 0.125$	$\Delta\rho_{min} = -0.143$ e Å^{-3}
$S = 1.066$	Extinction correction: *SHELXL97*
1466 reflections	Extinction coefficient: 0.066 (14)
110 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
H atoms: see below	
$w = 1/[\sigma^2(F_o^2) + (0.0610P)^2 + 0.0766P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 4. *Selected geometric parameters (Å, °) for (III)*

C1—C1^{i}	1.480 (3)	C2—C21	1.5208 (19)

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

In all cases, rather large crystals were used because the specimens turned out to be very brittle and cracked into tiny pieces when we tried to cut them. All H atoms were located by difference syntheses and refined with fixed individual displacement parameters using a riding model [C—H(aromatic) = 0.93, C—H(secondary) = 0.97 and C—H(tertiary) = 0.98 Å], except for the hydroxyl H atoms in (I), whose coordinates were refined. As compound (II) contains only C, H and O atoms, and Mo $K\alpha$ radiation was used, its absolute structure could not be determined.

For all compounds, data collection: *DIF*4 (Stoe & Cie, 1984*a*); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1984*b*); program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97.

We thank Professor Dr M. Lüttke (University of Göttingen) for providing us with the samples, Professor Dr E. Egert (University of Frankfurt) for helpful discussions and the Deutsche Forschungsgemeinschaft for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1161). Services for accessing these data are described at the back of the journal.

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6-Amino-9-(carboxymethyl)-2-methoxypurine Methyl Ester†

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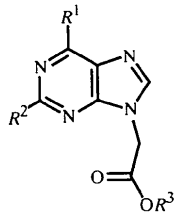
Abstract

The hydrogenolysis of 6-azido-9-(carboxymethyl)-2-methoxypurine methyl ester, (3), formed in a single step from 2,6-dichloro-9-(carboxymethyl)purine ethyl ester, (2), gave the title compound, $C_9H_{11}N_5O_3$, (1). The side chain attached at N9 avoids steric hindrance with the heterocycle by emerging almost orthogonally [C8—N9—C10—C11 −104.5 (2)°] and the amino group at N6 donates intermolecular hydrogen bonds to the ring N1 and ester carbonyl O11 atoms.

Comment

2,6-Dichloro-9-(carboxymethyl)purine ethyl ester, (2) (Chan *et al.*, 1995), with its displaceable Cl atoms, has provided a useful building block for the synthesis of base-modified intermediates (Sood *et al.*, 1997*a*,*b*) for incorporation into peptidic nucleic acids (Hyrup & Nielsen, 1996). At elevated temperatures, prolonged treatment of (2) in the presence of excess sodium azide, acetone and methanol yields predominantly 2,6-diazido-9-(carboxymethyl)purine ethyl ester through displacement of both chloro groups by azide. Two minor by-products arise from transesterification *in situ*, *i.e.* the methyl ester homologue (Sood *et al.*, 1997*a*) and a second methyl ester bearing one azido group and one methoxyl group attached at the heterocyclic ring. Hydrogenolysis of the methoxyl-containing intermediate converted the azido group to an amino group giving compound (1). We undertook the crystal structure determination of (1) to unambiguously establish the substitution pattern at the heterocyclic ring. This revealed that the amino and methoxyl groups were attached at C6 and C2, respectively, in (1) and that the azido group was attached at C6 in the precursor (3).

† Alternative name: methyl 6-amino-2-methoxypurine-9-acetate.



(2) $R^1 = R^2 = Cl; R^3 = CH_2CH_3$
(3) $R^1 = N_3; R^2 = OCH_3; R^3 = CH_3$
(1) $R^1 = NH_2; R^2 = OCH_3; R^3 = CH_3$

In the crystal structure, (1) exhibits none of the disorder apparent in the ethyl ester analogue where an amino group replaces the methoxyl group at C2 (Sood *et al.*, 1997*b*). Like other purine analogues containing methyl and ethyl acetate fragments attached at N9, the side chain in (1) avoids steric hindrance with the heterocycle by emerging almost orthogonally [C8—N9—C10—C11 −104.5 (2)°]. The atoms of the purine ring system are essentially coplanar within ±0.011 (1) Å. The methyl group at O2 eclipses N3, with N3—C2—O2—C14 1.7 (2)°.

The amino group is involved in two weak hydrogen bonds, creating centrosymmetric dimers that are further linked along the screw axis (Table 2).

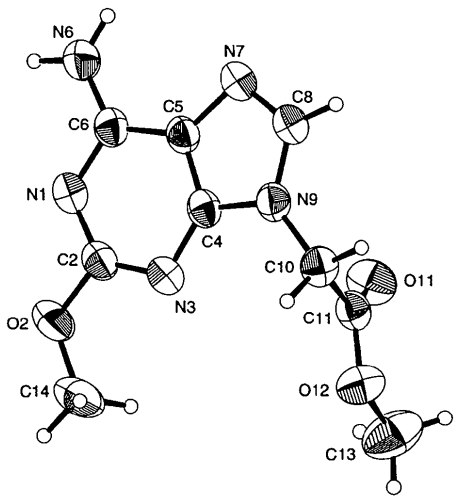


Fig. 1. *ORTEP*II view (Johnson, 1976) of the molecule of (1) with its numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

Experimental

The title compound (1) was obtained on catalytic hydrogenolysis of (3) using a method analogous to that described previously (Sood *et al.*, 1997*b*). Recrystallization was from ethyl acetate–methanol solution.

Crystal data

$C_9H_{11}N_5O_3$
M_r = 237.23
Cu $K\alpha$ radiation
λ = 1.54178 Å
Monoclinic
$P2_1/n$
a = 11.085 (3) Å
b = 7.7168 (6) Å
c = 13.006 (2) Å
β = 99.97 (2)°
V = 1095.8 (3) Å^3
Z = 4
D_x = 1.438 Mg m^{-3}
D_m not measured
Cell parameters from 25 reflections
θ = 23.5–37.9°
μ = 0.947 mm^{-1}
T = 293 (2) K
Plate
0.40 × 0.40 × 0.07 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North *et al.*, 1968)
T_{min} = 0.85, T_{max} = 0.94
2486 measured reflections
1946 independent reflections
1818 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
θ_{max} = 66.94°
$h = -2 \rightarrow 13$
$k = 0 \rightarrow 9$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.101
S = 1.381
1946 reflections
163 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 0.1761P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.175 e Å^{-3}
$\Delta\rho_{min}$ = −0.163 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0071 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C2—O2	1.346 (2)	C11—O11	1.200 (2)
C6—N6	1.330 (2)		
N3—C2—N1	129.50 (13)	N1—C6—C5	117.79 (13)
N3—C2—O2—C14	1.7 (2)	N9—C10—C11—O11	31.5 (2)
N1—C2—O2—C14	−179.48 (15)	O11—C11—O12—C13	−0.8 (2)
C8—N9—C10—C11	−104.5 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N6—H61···O11^i	0.89 (2)	2.26 (2)	3.111 (2)	160 (2)
N6—H62···N1^{ii}	0.91 (2)	2.15 (2)	3.055 (2)	171 (2)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, 1 - y, 1 - z$.

H-atom treatment: N—H free, rigid methyl H atoms and others riding.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CADABS* (Gould & Smith, 1986). Program(s) used to solve structure: *MULTAN*84 (Main *et al.*, 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.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1235). Services for accessing these data are described at the back of the journal.

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6,6′-Dimethyl-2,2′-bipyridyl

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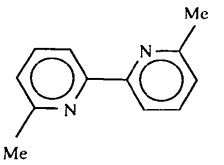
Abstract

In the solid state, the novel ligand 6,6′-dimethyl-2,2′-bipyridyl (dmbp), $C_{12}H_{12}N_2$, is a planar centrosymmetric molecule in which the pyridyl N atoms have a *transoid* arrangement, by virtue of the symmetry.

Comment

Square-planar complexes of Pt^{II} containing the title dmbp ligand, *e.g.* [Pt(dmbp)Cl_2], have aroused much interest recently due to their unusual redox and physical properties (Zuleta *et al.*, 1990; Miskowski *et al.*, 1993). Knowledge of the solid-state structure of this ligand will enable further understanding of its chemical behaviour and coordination ability.



dmbp

The molecule crystallizes in the space group $P2_1/c$, lying on a centre of symmetry, with the N atoms of the pyridyl rings *trans* to each other around the central bond. This conformation of the uncoordinated molecule contrasts with the *cisoid* arrangement necessary when it acts as a chelating ligand. The molecule is planar, with only the methyl H atoms deviating significantly from the plane. Bond lengths and angles are as expected for this type of system and compare favourably with those reported for other bipyridyl molecules (Nakatsu *et al.*, 1972; Troyanov *et al.*, 1989).

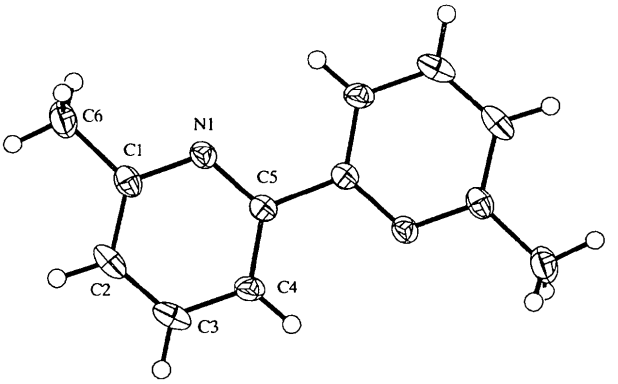


Fig. 1. The molecular structure of dmbp shown with 50% probability ellipsoids.

Experimental

The title compound was prepared according to the method of Badger & Sasse (1956, 1963), with modifications (Case, 1966; Burstal, 1938; Parks *et al.*, 1973; Newcome *et al.*, 1981; Rodde & Breitmaier, 1987) in order to improve yield. 2-Picoline (Aldrich) was refluxed (96 h) over freshly degassed Raney-nickel catalyst (dried under vacuum for 3 h) using a Soxhlet apparatus. NaOH was added to the alloy at 353–363 K over a period of 15 min. After removal of unreacted 2-picoline by distillation, the crude product was dissolved in ethanol, heated to boiling point and filtered over decolourising charcoal. The resulting yellow solution was evaporated to dryness and sublimed at 373 K. Recrystallization from ethanol produced clear prismatic crystals, which were characterized by NMR using a Bruker AMX360 (DMSO-d_6); δ 2.52 (*s*, py-CH_3, 6H), 7.25 (*d*, 5,5′-py-H, J = 7.5 Hz, 2H), 7.76 (*t*, 4,4′-py-H, J = 7.7 Hz, 2H) and 8.14 (*d*, 3,3′-py-H, J = 7.8 Hz, 2H).