Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Benzyl 2-amino-6-chloro-9*H*-purine-9-carboxylate

Kassim F. Adebambo, Nicola M. Howarth and Georgina M. Rosair*

Chemistry, William Perkin Building, School of Engineering & Physical Sciences, Heriot–Watt University, Riccarton, Edinburgh EH14 4AS, Scotland

Correspondence e-mail: g.m.rosair@hw.ac.uk

Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.034
wR factor = 0.095
Data-to-parameter ratio = 14.8

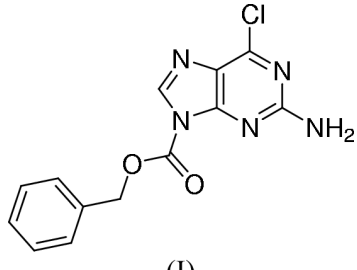
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 8 December 2004
Accepted 19 January 2005
Online 29 January 2005

The title compound, $C_{13}H_{10}ClN_5O_2$, crystallizes with two molecules in the asymmetric unit. These are connected by five hydrogen bonds, *viz.* three N—H···N interactions, two longer C=O···H—N interactions, bifurcated at the O atom, and a C—H···N contact.

Comment

The chemistry of purines has been largely driven in recent years by the desire to synthesize oligonucleotides and their analogues as well as novel purine-containing nucleosides for a wide range of medicinal applications (Vyle & Howarth, 2001). We have previously reported the synthesis and polymerization of lipophilic polyamide nucleic acids (PNA) as potential colorimetric diagnostics (Howarth, Lindsell *et al.*, 2003), and the design and synthesis of true peptide mimics of DNA for possible use as antigene agents (Howarth & Wakelin, 1997; Howarth, Wakelin & Walker, 2003). During these studies, we have encountered numerous difficulties in preparing the required *N*-2-benzyloxycarbonyl-protected guanine monomers from 2-amino-6-chloropurine (Howarth & Wakelin, 1997). Inspired by the work reported by Dey & Garner (2000) on the synthesis of tris-*tert*-butoxycarbonyl 2-amino-6-chloropurine, we decided to employ a similar strategy for preparing these monomers. As had been found by Dey & Garner (2000), this reaction afforded a single product. However, analysis of the product by ^{1}H NMR spectroscopy showed the presence of only one benzyloxycarbonyl group rather than three, which had been the case when 2-amino-6-chloropurine was treated with di-*tert*-butyl dicarbonate under analogous conditions (Dey & Garner, 2000). The exact identity of the monobenzyloxycarbonyl-protected product was revealed to be that of the title compound, (I), by a single-crystal X-ray study.



(I)

Compound (I) crystallizes as two crystallographically independent molecules (*A* and *B*) (Fig. 1). These differ in the relative ring orientations about the C10—N9 bonds [C4*A*—N9*A*—C10*A*—O10*A* = −5.0 (2)° and C4*B*—N9*B*—C10*B*—

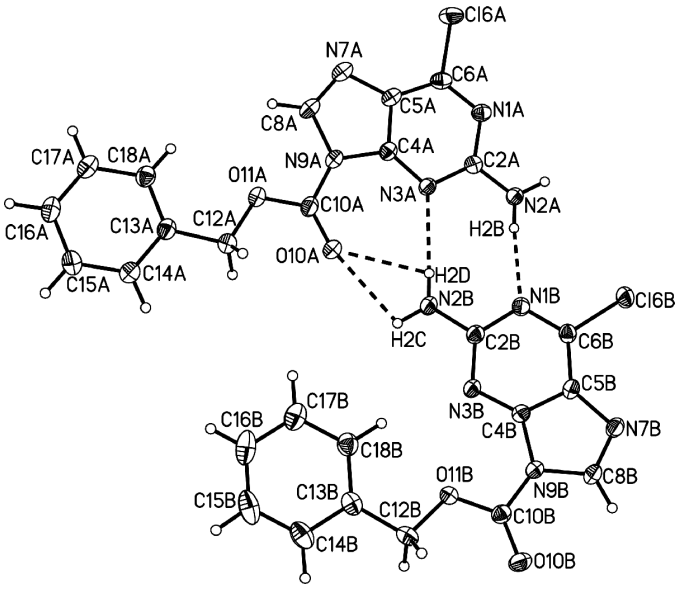


Figure 1
Perspective view of the asymmetric unit in (I), with hydrogen bonds shown as dashed lines. Displacement ellipsoids are shown at the 50% probability level and H atoms have arbitrary radii of 0.1 Å for clarity.

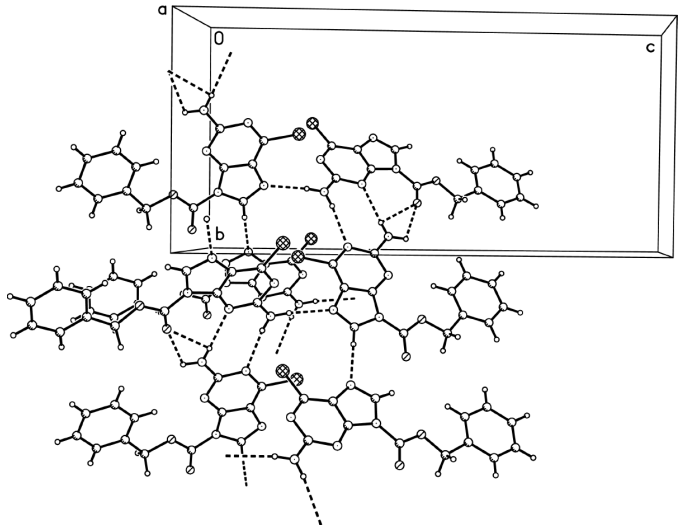


Figure 2
View of the packing arrangement for (I). Dashed lines indicate hydrogen bonds.

O10*B* = −173.60 (13)°]. The independent molecules *A* and *B* have different hydrogen-bonding arrangements. There is extensive hydrogen bonding between the two crystallographically independent molecules. They are connected by five intermolecular hydrogen bonds [N2*A*—H2*B*···N1*B*, N2*B*—H2*D*···N3*A*, N2*B*—H2*C*···O10*A*, N2*B*—H2*D*···O10*A* and N2*A*—H2*B*···N7*B*^{i} [symmetry code: (i) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$; Table 1], where the N—H···N contacts are the shortest. The first four hydrogen bonds are shown in Fig. 1. The hydrogen-bonding links between molecules *A* and *B* result in the formation of two eight-membered rings. The N—H···N contacts have a symmetrical carboxylic acid dimer motif, $R_2^2(8)$ (Bernstein *et al.*, 1995). The geometry of the N—H···O contact is very different, the angles at H2*C* and H2*D* being 101.6 (13) and 101.1 (13)°, respectively. The fifth intermolecular contact is another N—H···N contact, N2*A*—H2*B*···N7*B*^{i}, which is almost parallel to the *c* axis and gives rise to an infinite chain that runs parallel to the *b* axis, shown in Fig. 2. However, N7*A* does not take part in such a close intermolecular contact. The closest contact for N7*A* is C8*B*—H8*B*···N7*A*^{ii} [symmetry code (ii) $1+x, 1+y, z$].

Experimental

Dibenzyl dicarbonate (2.40 ml, 9.42 mmol, 4 equivalents) was added to a stirred solution of 2-amino-6-chloropurine (0.40 g, 2.36 mmol, 1 equivalent) and DMAP (dimethylaminopyridine, 0.03 g, 0.1 equivalent) in anhydrous dimethylformamide (50 ml) at room temperature under argon, and the resulting mixture was left to stir for 18 h. Subsequently, the solvent was removed *in vacuo* and the residue was purified by column chromatography using ethyl acetate/petroleum ether (2:1) as the eluting solvent. The product-containing fractions were combined to afford a brown oily solid, which was further purified by trituration with diethyl ether to give (I) as a colourless solid (yield 0.80 g, 26%). Compound (I) was crystallized from deuterochloroform. M.p. 417–418 K; R_f 0.35 (ethyl acetate/petroleum ether, 2:1). Analysis found: C 51.18, H 3.32, N 22.95%; $C_{13}H_{10}O_2N_5Cl$ requires: C 51.41, H 3.32, N 23.06%. ν max (KBr, cm^{-1}): 3497, 3313, 3198, 1775, 1742, 1626, 1561, 1512, 1485, 1395, 1368, 1301, 1192, 1175 and 1107; ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.49 (*s*, 2H), 5.64 (*br s*, 2H), 7.34–7.53 (*m*, 5H), 8.23 (*s*, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 70.2, 128.8, 129.2, 133.5, 139.6, 147.2, 152.4, 153.0, 160.4. NMR spectra were recorded on Bruker DPX400 and AC200 spectrometers, from $CDCl_3$ solutions at 293 K.

Crystal data

$C_{13}H_{10}ClN_5O_2$	D_x = 1.529 Mg m^{-3}
M_r = 303.71	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 7840 reflections
a = 9.2724 (5) Å	θ = 2.2–27.4°
b = 11.7943 (6) Å	μ = 0.30 mm^{-1}
c = 24.4404 (11) Å	T = 100 (2) K
β = 99.180 (2)°	Block, colourless
V = 2638.6 (2) Å^3	0.20 × 0.16 × 0.14 mm
Z = 8	

Data collection

Bruker–Nonius APEX2 CCD area-detector diffractometer	6497 independent reflections
φ and ω scans	5110 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	R_{int} = 0.050
T_{min} = 0.942, T_{max} = 0.959	θ_{max} = 28.2°
90 190 measured reflections	$h = -12 \rightarrow 12$
	$k = -15 \rightarrow 15$
	$l = -32 \rightarrow 32$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.5642P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.034	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.095	$\Delta\rho_{max}$ = 0.31 e Å^{-3}
S = 1.08	$\Delta\rho_{min}$ = −0.26 e Å^{-3}
6497 reflections	
440 parameters	
Only H-atom coordinates refined	

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2A—H2A···N7B^{i}	0.890 (17)	2.197 (17)	3.0771 (17)	169.9 (14)
N2A—H2B···N1B	0.861 (17)	2.212 (18)	3.0634 (16)	169.9 (15)
N2B—H2D···N3A	0.836 (18)	2.302 (19)	3.1378 (17)	177.8 (17)
N2B—H2D···O10A	0.836 (18)	2.464 (17)	2.7501 (15)	101.1 (13)
N2B—H2C···O10A	0.886 (18)	2.432 (17)	2.7501 (15)	101.6 (13)
C8B—H8B···N7A^{ii}	0.915 (17)	2.375 (17)	3.2779 (18)	169.1 (14)

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

The coordinates of all H atoms were refined freely, whilst the isotropic displacement parameters were treated as riding on the bound atom such that U_{iso}(H) = 1.2U_{eq}(C,N).

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

The authors thank Christina Graham for micro-analysis and the European Commission Framework 6 programme (project ref. LSHB-CT-2003-503480) for funding.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (1998). *SHELXTL* (Version 5.1) and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2003). *APEX2*. Version 1.0-8. Bruker AXS Inc., Madison, Wisconsin, USA.
Dey, S. & Garner, P. (2000). *J. Org. Chem.* **65**, 7697–7699.
Howarth, N. M., Lindsell, W. E., Murray, E. & Preston, P. N. (2003). *Tetrahedron Lett.* **44**, 8089–8092.
Howarth, N. M. & Wakelin, L. P. G. (1997). *J. Org. Chem.* **62**, 5441–5450.
Howarth, N. M., Wakelin, L. P. G. & Walker, D. M. (2003). *Tetrahedron Lett.* **44**, 695–698.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
Vyle, J. S. & Howarth, N. M. (2001). *Specialist Periodical Reports*, *Organophosphorous Chemistry*, Vol. 31, edited by D. W. Allen & J. C. Tebby, pp. 135–218. London: Royal Society of Chemistry.