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Structure of Benzyl 6-Aminopurine-9-carboxylate*

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Abstract. $C_{13}H_{11}N_5O_2$, orthorhombic, $Pca2_1$, $a = 12{\cdot}426$ (4), $b = 6{\cdot}528$ (2), $c = 30{\cdot}580$ (5) Å ($T = 295 \pm 3$ K), $V = 2480{\cdot}4$ Å^3, $Z = 8$ (two per asymmetric unit), $M_r = 269$, λ(Cu $K\alpha$) = 1·54051 Å, D_m (flotation) = 1·45, $D_x = 1{\cdot}44$ Mg m^{-3}, μ(Cu $K\alpha$) = 0·60 mm^{-1}, $R = 0{\cdot}058$ for 2557 reflections ($I > 2\sigma$). Molecule I is connected to molecule II by a pair of hydrogen bonds using the Watson–Crick sites N(1) and N(6). In addition, molecules I and II are linked by a single N(6)—H···N(7) hydrogen bond involving the Hoogsteen sites. The bases hydrogen bonded using Watson–Crick sites are parallel and those using Hoogsteen sites are inclined at 60° to one another.

Introduction. Reaction products of chloroformates with adenine serve as useful intermediates in the synthesis of naturally occurring ureidopurine derivatives. This structural study was undertaken to settle the assignments of the sites of acylation by chloroformates (Ohrt, Srikrishnan, Parthasarathy, Dutta & Chheda, 1978).

Crystals of the title compound were obtained by a slow evaporation from chloroform. 2866 reflections (309 had intensities $<2\sigma$) to the limit of $2\theta = 165°$ for Cu $K\alpha$ were collected using the stationary-crystal–stationary-counter procedure (Furnas & Harker, 1955) and were processed in the usual way. The difference in absorption as a function of φ (Furnas, 1957) was measured for the axial reflections and used for correcting for the anisotropy of absorption.

The crystal structure was solved by application of the multi-solution technique using *MULTAN* (Germain, Main & Woolfson, 1971). After futile attempts to solve the structure in the centrosymmetric space group *Pcam* (as suggested by the near-centrosymmetric distribution of normalized structure factors), the structure was solved readily in the noncentrosymmetric space group $Pca2_1$, and refined by least squares with a block-diagonal approximation. The H atoms were located from difference electron density maps and their parameters were refined isotropically. The refinement was carried out by minimizing $\sum w[|F_o| - (1/k)|F_c|]^2$ and the observations were weighted by $1/f_C$ where f_C is the scattering factor for C. Atomic scattering factors for C, N and O were taken from *International Tables for X-ray Crystallography* (1968) and for H from Stewart, Davidson & Simpson (1965). The final R factor is 0·058 for the 2557 reflections ($I > 2\sigma$). The final atomic coordinates are given in Tables 1‡ and 2.

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[*] Hydrogen Bonding of Modified Adenines Involving Watson–Crick Sites.

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[‡] Lists of structure factors, anisotropic thermal parameters and bond distances and angles for the two molecules have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34507 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* ($\times 10^4$) *with estimated standard deviations in parentheses*

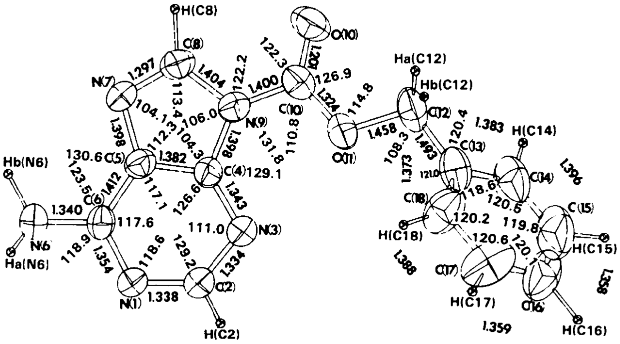
The coordinates of molecules I and II are related by approximate relations $x_1 + x_2 \simeq 0{\cdot}25, y_1 + y_2 \simeq 0{\cdot}5, z_1 + z_2 \simeq 1{\cdot}25$.

	x	y	z
Molecule I			
O(10)	544 (4)	2077 (6)	5450 (1)
O(11)	2087 (3)	3865 (6)	5397 (1)
N(1)	1767 (3)	10441 (6)	6335 (1)
N(3)	2263 (3)	7542 (6)	5885 (2)
N(6)	73 (4)	10860 (7)	6643 (2)
N(7)	−517 (3)	6836 (7)	6191 (1)
N(9)	732 (3)	5150 (7)	5789 (1)
C(2)	2436 (4)	9330 (8)	6086 (2)
C(4)	1241 (4)	6907 (7)	5952 (2)
C(5)	461 (4)	7886 (7)	6193 (2)
C(6)	753 (4)	9750 (7)	6392 (1)
C(8)	−333 (4)	5230 (8)	5956 (2)
C(10)	1096 (4)	3538 (8)	5536 (2)
C(12)	2505 (6)	2294 (8)	5102 (2)
C(13)	3570 (5)	3007 (9)	4930 (2)
C(14)	3679 (5)	4886 (12)	4726 (3)
C(15)	4665 (6)	5443 (15)	4538 (3)
C(16)	5513 (6)	4176 (16)	4557 (2)
C(17)	5395 (7)	2304 (15)	4741 (3)
C(18)	4446 (6)	1722 (11)	4936 (3)
Molecule II			
O(10)	2031 (3)	2976 (6)	7973 (1)
O(11)	490 (3)	1146 (6)	8017 (1)
N(1)	857 (3)	−5398 (6)	7087 (1)
N(3)	362 (3)	−2513 (6)	7532 (1)
N(6)	2548 (4)	−5805 (7)	6781 (2)
N(7)	3132 (3)	−1772 (7)	7234 (1)
N(9)	1869 (3)	−80 (6)	7616 (1)
C(2)	185 (4)	−4292 (8)	7331 (2)
C(4)	1369 (4)	−1867 (7)	7473 (2)
C(5)	2156 (3)	−2837 (7)	7227 (2)
C(6)	1875 (4)	−4709 (7)	7023 (2)
C(8)	2925 (4)	−166 (8)	7472 (2)
C(10)	1494 (4)	1513 (7)	7892 (2)
C(12)	30 (6)	2685 (9)	8305 (2)
C(13)	−994 (5)	1867 (9)	8487 (2)
C(14)	−1899 (6)	3098 (11)	8491 (2)
C(15)	−2836 (6)	2458 (13)	8697 (3)
C(16)	−2877 (6)	521 (15)	8872 (2)
C(17)	−1999 (6)	−729 (12)	8862 (2)
C(18)	−1064 (5)	−85 (10)	8647 (2)

Table 2. *Final atomic coordinates* ($\times 10^3$) *for the hydrogen atoms with their estimated standard deviations in parentheses*

	x	y	z
Molecule I			
H(C2)	305 (4)	999 (8)	598 (2)
H(C8)	−108 (5)	433 (9)	585 (2)
H*a*(N6)	16 (4)	1214 (8)	668 (2)
H*b*(N6)	−74 (6)	1030 (13)	672 (3)
H*a*(C12)	260 (7)	114 (13)	529 (3)
H*b*(C12)	186 (7)	210 (13)	485 (3)
H(C14)	332 (7)	620 (13)	479 (3)
H(C15)	463 (6)	697 (12)	440 (2)
H(C16)	631 (6)	467 (14)	442 (2)
H(C17)	605 (7)	125 (13)	469 (3)
H(C18)	423 (6)	48 (12)	496 (3)
Molecule II			
H(C2)	−59 (4)	−500 (81)	728 (2)
H(C8)	322 (5)	120 (10)	747 (2)
H*a*(N6)	225 (6)	−679 (12)	660 (2)
H*b*(N6)	305 (4)	−519 (8)	608 (2)
H*a*(C12)	61 (4)	278 (8)	854 (2)
H*b*(C12)	−6 (5)	399 (10)	811 (2)
H(C14)	−174 (6)	451 (11)	835 (2)
H(C15)	−347 (9)	345 (18)	876 (3)
H(C16)	−344 (6)	33 (11)	900 (2)
H(C17)	−224 (9)	−260 (15)	886 (3)
H(C18)	−50 (5)	−91 (11)	865 (2)

Discussion. This study together with the N(7) substituted analog (Ohrt *et al.*, 1978) constitutes the first unequivocal assignments of the structures of N^7- and N^9-acylated adenines. The molecular dimensions (Fig. 1) correspond to those found in other similar molecules. For most of the bonds, the values for molecules I and II are within 2σ.* In some cases, the differences in bond lengths are pronounced, though no reason is apparent. It is possible that the approximate relationship among the coordinates (see Table 1) gives rise to high correlations. As can be seen from Fig. 1, the two molecules in the asymmetric unit are very similar, with the phenyl ring twisted from the planes of the base and the acyl group by different amounts [the torsion angles O(11)—C(12)—C(13)—C(14) are ∓54·7 and ±45·2° for the two molecules]. The keto O atom of the N(9) acyl group is *cis* to C(8) in both molecules (Fig. 1) and assumes the preferred conformation for esters across the C—O bond (Mathieson, 1965).



	I	II
C(8)—N(9)—C(10)—O(11)	± 176	∓ 174
N(9)—C(10)—O(11)—C(12)	∓ 176	± 180
C(10)—O(11)—C(12)—C(13)	± 173	∓ 169
O(11)—C(12)—C(13)—C(14)	∓ 55	± 45

Fig. 1. Structure of benzyl 6-aminopurine-9-carboxylate. The keto oxygen of the N(9) acyl group is *cis* to C(8) in both the molecules in the crystallographic asymmetric unit. The mean values of the bond distances (Å) and angles (°) and selected torsion angles (°) are also given. The average e.s.d.'s are: for bond lengths 0·007 Å, for bond angles 0·5°, and for torsion angles given in this figure 0·5°.

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* See deposition footnote.

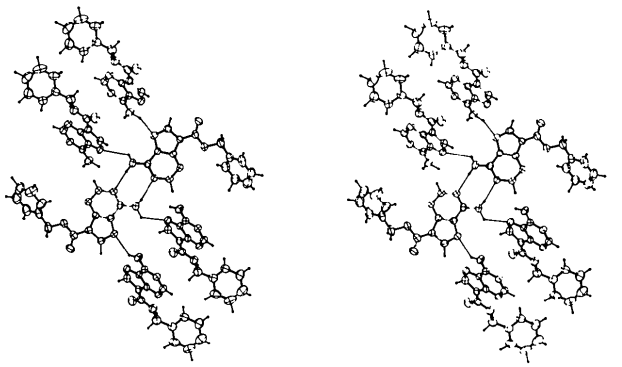

Fig. 2. Stereoscopic view of the hydrogen bonding in the crystal structure. Molecule I is drawn with open bonds and molecule II with solid bonds. N(6) of molecule I is connected to II by N(6)–H···N(1) hydrogen bonding [H···N(1) 2·21 (5) Å, ∠N(6)–H(6)···N(1) 147 (5)°], and by a single N(6)–H(N6)···N(7) hydrogen bond [H···N(7) 2·32 (8) Å, ∠N(6)–H(N6)···N(7) 125 (6)°]. N(6) of molecule II is hydrogen bonded to N(1) and N(7) of two molecules of type I [H···N(1) 2·07 (8) Å, ∠N(6)–H(N6)···N(1) 163 (7)°; H···N(7) 2·57 (5) Å, ∠N(6)···H(N6)···N(7) 125 (5)°].

The hydrogen-bonding scheme is illustrated in Fig. 2 and the hydrogen-bond lengths and angles are also given in the same figure. Molecules I and II are connected by a pair of N(6)–H(N6)···N(1) hydrogen bonds using the Watson–Crick sites N(1) and N(6). These two molecules are almost parallel to each other. In addition, molecule I is also linked to another molecule II by a single N(6)–H(N6)···N(7) type of hydrogen bond, which involves the Hoogsteen sites. These two molecules are inclined to each other by 60° in contrast to those bonded by Watson–Crick sites which are parallel to each other. It is interesting to note that one adenine is involved in hydrogen-bonding interactions with three others, thereby forming a quadruple interaction. The keto O(10) atom of the acyl group does not take part in any hydrogen bonding. The molecules are arranged in such a way that there is a partial overlap of the adenine rings, and also overlap of the adenine rings with the phenyl rings.

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Structure du Complexe Ervistine–Méthanol

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Abstract. $C_{19}H_{20}N_2O.CH_3OH$, M_r = 324, orthorhombic, $P2_12_12_1$, a = 7·515 (4), b = 15·650 (9), c = 15·857 (8) Å, V = 1864·8 Å^3, D_c = 1·15 Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å. The structure has been solved by direct methods using diffractometer data and refined to R = 0·04 for 1602 observed reflections. The stereochemistry of this alkaloid extracted from *Pandaca boiteaui* (Apocynaceae) has been established. Hydrogen bonds involving methanol connect two molecules of ervistine.

Introduction. L'ervistine (3) est un alcaloïde d'un type nouveau extrait des écorces de *Pandaca boiteaui* (Apocynacées) récoltées à Madagascar. Les cristaux,

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