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9-(Carboxymethyl)-6-chloropurine Ethyl Ester†

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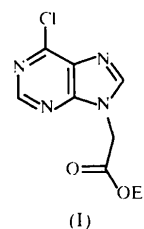
Abstract

Alkylation of 6-chloropurine using ethyl bromoacetate gives a mixture of monoalkyl regio-isomers from which the title compound, C₉H₉ClN₄O₂, was isolated in crystalline form. In both independent molecules, the side chain adopts an extended conformation; its carboxymethyl-group plane intersects the planar heterocycle at angles of 60.1 (1) and 65.8 (1)°, respectively.

Comment

The synthetic usefulness of *N*-substituted chloropurines is well documented; displacement of the chloro group can be achieved using amine or oxygen nucleophiles to provide adenine and hypoxanthine analogues with defined substitution patterns. This route, particularly to substituted hypoxanthines, is preferred (Rao & Revankar, 1995) since direct alkylation of hypoxanthine itself gives mixtures containing peralkylated products (Sood

et al., 1998a). Although direct alkylation of 6-chloropurine attaches a substituent at either N9 or N7, alkylation occurs predominantly at N9 in the absence of protecting groups (Dalby *et al.*, 1993). The distribution of regio-isomers is similar, whether potassium carbonate (Sood *et al.*, 1998c) or sodium hydride (Rao & Revankar, 1995) is used as the base. Alkylation of 6-chloropurine using ethyl bromoacetate gave a separable mixture of crystalline regio-isomeric products: 7-(carboxymethyl)-6-chloropurine ethyl ester, (II), in 27% yield, and the title compound, (I), in 65% yield. Although we have already reported on the crystal structure of (II) (Sood *et al.*, 1998c), only recently did we obtain X-ray diffraction quality crystals of its regio-isomer, (I). We decided to determine the crystal structure of (I) in order to illustrate that the ethyl acetate side chain was indeed attached at N9 as anticipated, and also to compare the structure of (I) with its regio-isomer, (II), and related structures.



Two molecules, (IA) and (IB), constitute the asymmetric unit. The ethyl acetate side chain in (I) avoids steric hindrance with the heterocycle by emerging from N9 with the C8—N9—C10—C11 torsion angle equal to 58.2 (5)° in (IA) and 65.1 (5)° in (IB). In the reported series of substituted analogues containing the same ethyl acetate fragment (Sood *et al.*, 1997b; Flensburg & Egholm, 1994) or the methyl homologue (Sood *et al.*, 1997a, 1998b), the equivalent torsion angle ranges are 50.8 (6) to 104.65 (13) and –92.9 (3) to –104.5 (2)°, respectively. The ring atoms in (IA) and (IB) are planar, with r.m.s. deviations of 0.006 and 0.009 Å, respectively. Many of the geometrical features of (I) resemble those of its 2,6-dichloro analogue (Chan *et al.*, 1995), but with the internal N3—C2—N1 angle in (I) marginally compressed, by 1.8 (4)°. Compared with the regio-isomer, (II), attachment of the substituent at N9 expands the internal angles at C5 by 4.3 (4) and at N9 by 1.8 (4)°, whereas C4 and N7 are contracted by –4.2 (4) and –1.5 (4)°. The side chain in (I) differs from (II), both in its relationship to the heterocycle and in its conformation; torsion angles for (IA) and (IB) are given in Table 1, and show an almost fully extended conformation. In the absence of any amino groups, the most significant of several C—H...O contacts is a weak hydrogen bond between H8A and a nearby O12B' carbonyl group in the other independent molecule in the unit cell, with H8A...O12B' = 2.52 (2) Å [symmetry code: (i) –x + 1, –y, –z + 1].

† Alternative name: ethyl 6-chloropurine-9-acetate.

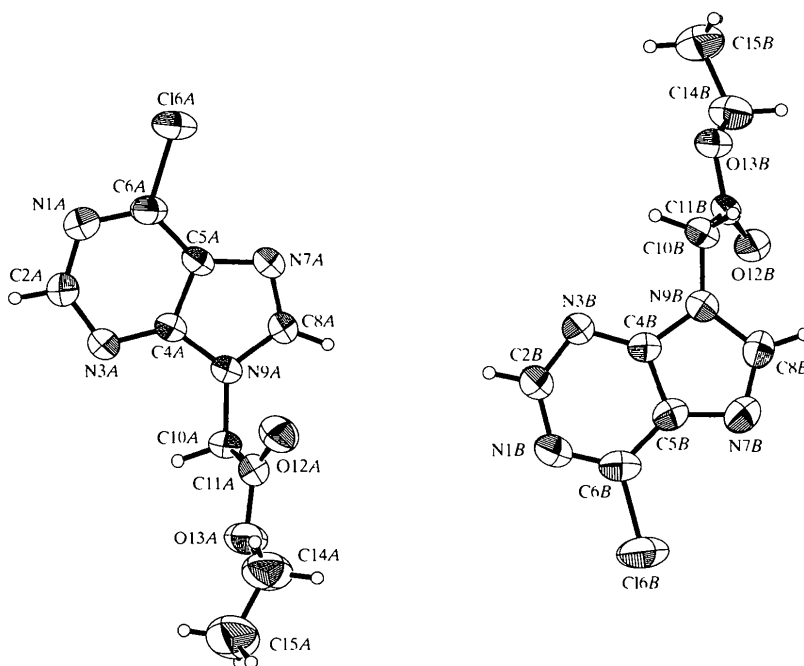


Fig. 1. ORTEP plot (Johnson, 1976), showing the structures of the two independent molecules of (I) and the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as spheres of arbitrary radii.

Experimental

The title compound, (I), was synthesized by direct alkylation of 6-chloropurine using ethyl bromoacetate and potassium carbonate in acetonitrile, as described recently by Sood *et al.* (1998c), and then recrystallized from methanol.

Crystal data

C₉H₉ClN₄O₂
M_r = 240.65
 Triclinic
 $P\bar{1}$
a = 5.872 (2) Å
b = 10.529 (2) Å
c = 19.096 (5) Å
 α = 105.01 (2)°
 β = 93.85 (2)°
 γ = 105.00 (2)°
V = 1090.1 (5) Å³
Z = 4
D_x = 1.466 Mg m⁻³
D_m not measured

Cu *K*α radiation
 λ = 1.54178 Å
 Cell parameters from 25 reflections
 θ = 19.7–33.2°
 μ = 3.066 mm⁻¹
T = 293 (2) K
 Prism
 0.35 × 0.15 × 0.10 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} = 0.473, T_{\max} = 0.736
 3890 measured reflections
 3826 independent reflections

3245 reflections with $I > 2\sigma(I)$
 R_{int} = 0.077
 θ_{max} = 67.92°
 $h = 0 \rightarrow 7$
 $k = -12 \rightarrow 12$
 $l = -22 \rightarrow 22$
 3 standard reflections
 frequency: 120 min
 intensity decay: 9%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.078$
 $wR(F^2) = 0.234$
 $S = 1.099$
 3659 reflections
 292 parameters
 H atoms riding
 $w = 1/[\sigma^2(F_o^2) + (0.1616P)^2 + 0.5288P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 0.597 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.627 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL93 (Sheldrick, 1993)
 Extinction coefficient: 0.0075 (16)
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

N7A—C8A	1.311 (5)	N7B—C8B	1.301 (6)
C8A—N9A	1.367 (4)	C8B—N9B	1.377 (5)
N3A—C2A—N1A	128.0 (3)	N3B—C2B—N1B	128.2 (3)
N9A—C4A—C5A	105.6 (3)	N9B—C4B—C5B	105.6 (3)
N7A—C5A—C4A	110.3 (3)	C6B—C5B—C4B	115.0 (3)
C8A—N7A—C5A	103.5 (3)	C8B—N7B—C5B	103.8 (3)
N7A—C8A—N9A	114.6 (3)	N7B—C8B—N9B	114.3 (3)
C4A—N9A—C8A	106.0 (3)	C4B—N9B—C8B	105.5 (3)
C8A—N9A—C10A—C11A		58.2 (5)	
N9A—C10A—C11A—O13A		174.6 (3)	
C10A—C11A—O13A—C14A		-176.6 (4)	
C11A—O13A—C14A—C15A		159.4 (5)	
C8B—N9B—C10B—C11B		65.1 (5)	
N9B—C10B—C11B—O13B		168.9 (3)	
C10B—C11B—O13B—C14B		-177.9 (3)	
C11B—O13B—C14B—C15B		169.1 (3)	

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: MULTAN11/84 (Main *et al.*, 1984). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics:

ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1279). Services for accessing these data are described at the back of the journal.

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4'-(Dimethylamino)-2-nitroazobenzene†

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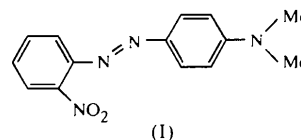
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Abstract

The title compound, C₁₄H₁₄N₄O₂, has *trans* geometry about the azo linkage. The dihedral angle between the two phenyl rings is 5.3(2)° and the twist angle for the nitro group is 63.9(2)°. Excluding the nitro group, the molecular skeleton is almost planar, which may enhance the photostability of the compound. Within the crystal structure, molecules related by a glide plane are connected by weak intermolecular hydrogen bonding and form zigzag chains in the [001] direction. The polar molecular chains, which are arranged anti-parallel, are packed into stacks in the [101] direction through $\pi \cdots \pi$ interactions; the interstack forces are mainly van der Waals interactions.

Comment

Dyes based on 4-aminoazobenzene, containing a donor-acceptor chromogen, are important for use on polyester fibres, owing to their desirable colour and satisfactory light-fastness properties (Jan *et al.*, 1984; Oh & Kim, 1995). Some push-pull azobenzene compounds are second- or third-order nonlinear optical materials (Kang *et al.*, 1995; Shen *et al.*, 1992) and have potential applications in photonic devices. Technical interest prompted us to undertake a systematic study (Zhang *et al.*, 1997), during the course of which we synthesized the title compound, (I), and confirmed its structure by X-ray analysis.



The bond distances in (I) are essentially the same when compared with those in 4'-(diethylamino)-2-nitroazobenzene [(II); Zhang *et al.*, 1997] and 4'-[bis(β -hydroxyethyl)amino]-2-nitroazobenzene [(III); McIn-tosh *et al.*, 1989)], apart from the short N1—O2 link [1.190(3), 1.217(2) and 1.221(2) Å for (I), (II) and

† IUPAC name: (4-dimethylaminophenyl)(2-nitrophenyl)diazene.