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Ethyl 9-Adeninylacetate at 122 K

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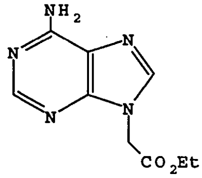
Abstract

The structure of the title compound, $C_9H_{11}N_5O_2$, at 122 K has been established by X-ray diffraction methods. The ethyl acetate moiety is virtually planar and almost perpendicular to the adenine ring system. Hydrogen bonds between the amino groups and two adenine N atoms connect the molecules in chains parallel to the *c* axis.

Comment

The title compound, (I), was isolated as a reaction intermediate in the preparation of the building blocks of PNA, the peptide analogue of DNA (Nielsen, Egholm, Berg & Buchardt, 1991; Egholm, Buchardt, Nielsen & Berg, 1992). Details of the preparation of the compound will be published elsewhere (Egholm *et al.*, 1994). The structure determination was undertaken to establish where the substitution in the adenine ring had occurred and to elucidate how a bulky substituent influences the hydrogen-bonding pattern. The molecular geometry is illustrated in Fig. 1 and by the bond lengths and angles in Table 2; these values are in excellent agreement with those found in other structures containing the adenine ring system (Stewart & Jensen, 1964; Lai & Marsh, 1972; Wilson, Tollin & Howie, 1986; Low, Tollin & Howie, 1987).



(I)

The structure determination revealed that the substitution had occurred at the 9 position. The ethyl acetate fragment adopts an extended conformation. The six atoms of this moiety are coplanar with a maximum deviation from the least-squares plane of 0.041 (1) Å for O31. This plane is almost perpendicular to the least-squares plane defined by the adenine ring system, the angle between the two planes being 84.46 (4)°, and the torsion angle C8—C9—C22—C21 being 104.65 (13)°. This conformation differs significantly from the one found for other substituents in this position; in adenosine (Lai & Marsh, 1972) the equivalent torsion angle is 9.9°. The two H atoms of the amine group are potential hydrogen-bond donors and as well as atoms N1, N3 and N7 of the adenine ring, O21 of the ethyl acetate fragment could also be a hydrogen-bond acceptor. However, the hydrogen-bonding pattern is similar to that found in 9-methyl adenine (Stewart & Jensen, 1964) with N16—H162···N1 and N16—H161···N7 hydrogen bonds connecting molecules related by translational symmetry along the *c* axis (Table 2, Fig. 2). The plane through the adenine ring is almost parallel to the *ab* plane and the side chains are oriented so that they fill the space between the adenine ring planes of neighbouring molecules.

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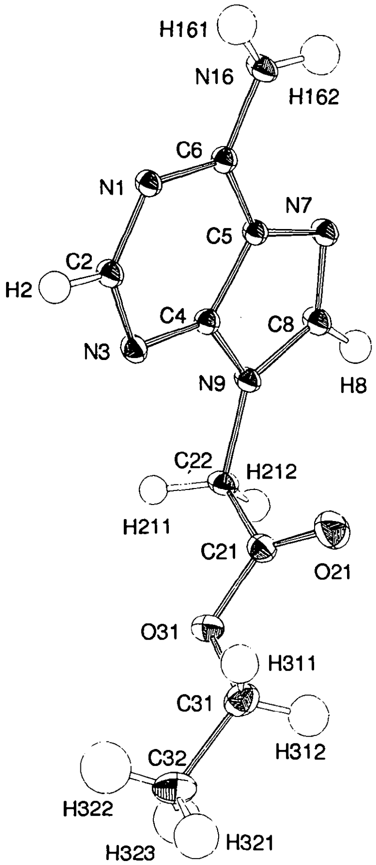

Fig. 1. View of ethyl 9-adeninylacetate showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level for all atoms.

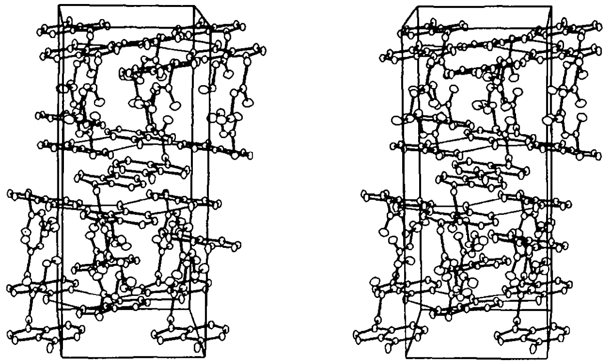

Fig. 2. Stereoscopic view of the crystal packing viewed along the *b* axis. The *a* axis is vertical. Hydrogen bonds are drawn as thin lines.

Experimental

The compound was synthesized as described by Egholm *et al.* (1994) and recrystallized from ethanol

Crystal data

$C_9H_{11}N_5O_2$
$M_r = 221.23$
Orthorhombic
Pbca
$a = 19.4943\ (15)$ Å
$b = 12.2427\ (7)$ Å
$c = 8.5428\ (5)$ Å
$V = 2038.8\ (2)$ Å^3
$Z = 8$
$D_x = 1.441$ Mg m^{-3}

Cu *Kα* radiation
$\lambda = 1.5418$ Å
Cell parameters from 22 reflections
$\theta = 38.99\text{–}46.16°$
$\mu = 0.898$ mm^{-1}
$T = 122\ (2)$ K
Parallelpiped
0.35 × 0.35 × 0.20 mm
Colourless

Data collection

CAD-4 diffractometer
Profile data from $\omega\text{–}2\theta$ scans
Absorption correction: none
6102 measured reflections
2105 independent reflections
1978 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0145$
$\theta_{\rm max} = 74.85°$
$h = -24 \rightarrow 24$
$k = -15 \rightarrow 15$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 166.7 min
intensity variation: 1.2%

Refinement

Refinement on F^2
$R(F) = 0.0318$
$wR(F^2) = 0.0856$
$S = 1.114$
2105 reflections
190 parameters
All H-atom parameters refined
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 1.0198P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 0.30\ (4)$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26\ (4)$ e Å^{-3}
Extinction correction: $F_c^* = kF_c[1 + (0.001x \times F_c^2\lambda^3/\sin 2\theta)]^{-1/4}$
Extinction coefficient: $x = 0.0066\ (3)$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N1	0.58396 (5)	0.37085 (8)	−0.10011 (11)	0.0156 (2)
C2	0.59014 (6)	0.47672 (9)	−0.13830 (13)	0.0161 (2)
N3	0.58984 (5)	0.56422 (8)	−0.04573 (11)	0.0159 (2)
C4	0.58102 (6)	0.53396 (9)	0.10430 (13)	0.0137 (2)
C5	0.57416 (6)	0.42890 (9)	0.16294 (13)	0.0140 (2)
C6	0.57671 (5)	0.34328 (9)	0.05282 (13)	0.0141 (2)
N7	0.56333 (5)	0.43186 (8)	0.32421 (11)	0.0170 (2)
C8	0.56467 (6)	0.53698 (9)	0.35777 (13)	0.0170 (2)
N9	0.57521 (5)	0.60254 (8)	0.23049 (11)	0.0151 (2)
N16	0.57088 (5)	0.23723 (8)	0.08934 (12)	0.0188 (2)
O21	0.70574 (5)	0.69397 (8)	0.23732 (12)	0.0296 (2)
C21	0.65844 (6)	0.74923 (10)	0.19587 (13)	0.0176 (2)
C22	0.58360 (6)	0.72016 (9)	0.22314 (14)	0.0166 (3)
O31	0.66365 (4)	0.84522 (7)	0.12226 (10)	0.0192 (2)
C31	0.73399 (6)	0.88396 (11)	0.0970 (2)	0.0241 (3)
C32	0.72915 (8)	0.99425 (12)	0.0213 (2)	0.0312 (3)

Table 2. *Selected geometric parameters* (Å, °)

N1—C2	1.3420 (14)	N7—C8	1.3188 (15)
N1—C6	1.3567 (14)	C8—N9	1.3670 (15)
C2—N3	1.3315 (15)	N9—C22	1.4506 (14)
N3—C4	1.3452 (14)	O21—C21	1.1973 (15)
C4—N9	1.3711 (14)	C21—O31	1.3367 (14)
C4—C5	1.3868 (15)	C21—C22	1.520 (2)
C5—N7	1.3942 (14)	O31—C31	1.4668 (14)
C5—C6	1.4093 (15)	C31—C32	1.500 (2)
C6—N16	1.3402 (14)		

C2—N1—C6	118.93 (10)	N1—C6—C5	117.48 (10)
N3—C2—N1	129.22 (10)	C8—N7—C5	103.72 (9)
N3—C2—H2	114.7 (9)	N7—C8—N9	113.77 (10)
N1—C2—H2	116.1 (9)	C8—N9—C4	106.15 (9)
C2—N3—C4	110.18 (9)	C8—N9—C22	129.36 (10)
N3—C4—N9	126.23 (10)	C4—N9—C22	124.37 (10)
N3—C4—C5	127.73 (10)	O21—C21—O31	125.27 (11)
N9—C4—C5	106.02 (9)	O21—C21—C22	124.18 (11)
C4—C5—N7	110.33 (10)	O31—C21—C22	110.55 (9)
C4—C5—C6	116.44 (10)	N9—C22—C21	110.33 (9)
N7—C5—C6	133.18 (10)	C21—O31—C31	115.12 (9)
N16—C6—N1	118.29 (10)	O31—C31—C32	107.19 (10)
N16—C6—C5	124.21 (10)		

C6—N1—C2—N3	−0.6 (2)	C6—C5—N7—C8	−177.89 (12)
N1—C2—N3—C4	−0.9 (2)	C5—N7—C8—N9	0.30 (13)
C2—N3—C4—N9	−177.06 (11)	N7—C8—N9—C4	0.12 (14)
C2—N3—C4—C5	1.1 (2)	N7—C8—N9—C22	−176.11 (11)
N3—C4—C5—N7	−177.76 (11)	N3—C4—N9—C8	178.00 (11)
N9—C4—C5—N7	0.70 (13)	C5—C4—N9—C8	−0.49 (12)
N3—C4—C5—C6	0.0 (2)	N3—C4—N9—C22	−5.5 (2)
N9—C4—C5—C6	178.48 (9)	C5—C4—N9—C22	175.98 (10)
C2—N1—C6—N16	−179.72 (10)	C8—N9—C22—C21	104.65 (13)
C2—N1—C6—C5	1.8 (2)	C4—N9—C22—C21	−70.96 (14)
C4—C5—C6—N16	−179.93 (11)	O21—C21—C22—N9	−28.5 (2)
N7—C5—C6—N16	−2.8 (2)	O31—C21—C22—N9	152.62 (9)
C4—C5—C6—N1	−1.5 (2)	O21—C21—O31—C31	−1.9 (2)
N7—C5—C6—N1	175.64 (12)	C22—C21—O31—C31	177.04 (9)
C4—C5—N7—C8	−0.61 (13)	C21—O31—C31—C32	−177.14 (10)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N16—H161···N7[i]	0.93 (2)	2.15 (2)	3.072 (1)	172.4 (14)
N16—H162···N1[ii]	0.91 (2)	2.08 (2)	2.976 (1)	166.3 (15)

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

Data collection: Enraf–Nonius CAD-4 software. Cell refinement: Enraf–Nonius CAD-4 software. Data reduction: *DREADD* (Blessing, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL* (Sheldrick, 1994). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1182). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Elucidation of the Mechanism of Transposition of Tricyclo[*m*.*n*.0.$0^{2,m+1}$]-alka-2,3,*m*+2-triol Derivatives: the Stereochemistry of *cis*-*anti*-*cis*-1-Acetoxytricyclo[7.3.0.$0^{2,7}$]dodecan-8-one

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Abstract

The crystal structure analysis of the title compound (8-oxotricyclo[7.3.0.$0^{2,7}$]dodec-1-yl acetate, $C_{14}H_{20}O_3$) shows that in the transposition reaction causing its formation, the relative positions of the protons at the ring junctions are maintained, demonstrating that the process is a concerted one. The conformation and relevant structural parameters of the molecule, as found in the crystal, are compared with those calculated by molecular mechanics for the isolated molecule, providing evidence that packing effects exert no significant influence on the molecular conformation.

Comment

During studies of new approaches for obtaining polycyclic cyclopentane derivatives (Jamart-Grégoire, Brosse, Ianelli, Nardelli & Caubère, 1991, 1993; Ianelli,

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