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Structure of the Cytokinin N^6-Benzyladenine, $C_{12}H_{11}N_5$

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Abstract. $M_r = 225{\cdot}3$, triclinic, $P\bar{1}$, $a = 4{\cdot}8975$ (4), $b = 8{\cdot}2924$ (7), $c = 13{\cdot}8301$ (11) Å, $\alpha = 98{\cdot}077$ (7), $\beta = 92{\cdot}519$ (7), $\gamma = 100{\cdot}244$ (7)°, $Z = 2$, $V = 545{\cdot}9$ Å^3, $T = 295$ K, D_m(flotation) $= 1{\cdot}380$, $D_x = 1{\cdot}370$ Mg m^{-3}, $F(000) = 236$, Cu $K\alpha_1$, $\mu = 0{\cdot}7267$ mm^{-1}, $\lambda = 1{\cdot}54060$ Å, final $R(F) = 0{\cdot}061$ for 1631 reflections. The adenine moiety is in the N(9)—H tautomeric form and the molecules are linked across the centre of inversion through N(6)—H···N(7) and N(9)—H···N(3) hydrogen bonds using the Hoogsteen sites. The conformational features agree with those proposed for active cytokinins.

Introduction. N^6-Benzyladenine (6BAN), a modified base, is closely related to the plant-growth hormone kinetin and has a morphological effect on tissue culture (Bonner & Varner, 1965). The X-ray analysis of the crystal structure of the present compound was undertaken as part of the research project on the structure and conformation of cytokinins. The structure of 6BAN is also of interest as a monosubstituted adenine derivative.

Experimental. Yellow plates (from methanol), 0·5 × 0·4 × 0·2 mm, $\theta/2\theta$ scan with line profile analysis (Grant & Gabe, 1978); Picker four-circle automatic diffractometer, graphite-monochromatized Cu $K\alpha$; data corrected for direct-beam polarization (Le Page, Gabe & Calvert, 1979) and Lorentz factor; unit-cell parameters determined from least-squares refinement of angle values for 45 reflections with $50 < \theta < 60°$. 3927 reflections with $\theta < 60°$ (1631 unique) included in refinement, $R_{int} = 0{\cdot}015$, no absorption correction; *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), anisotropic full matrix (Gantzel, Sparks & Trueblood, 1961), H (from ΔF synthesis) isotropic, final $R(F) = 0{\cdot}061$, $R_w(F) = 0{\cdot}061$, $w = 1/(C_1 + |F_o| + C_2|F_o|^2)$ where $C_1 = 0{\cdot}44$, $C_2 = 0{\cdot}023$ (Cruickshank, Bujosa, Lovell & Truter, 1961); IBM 370/155 computer at the Indian Institute of Technology, Madras, India; final refinement cycle $(\Delta/\sigma)_{max} = 1{\cdot}0$, $(\Delta/\sigma)_{mean} = 0{\cdot}2$; final $\Delta\rho$ map had no peaks $>0{\cdot}25$ e Å^{-3}; atomic scattering factors from *International tables for X-ray Crystallography* (1962); no correction for secondary extinction.

Discussion. Positional parameters and isotropic temperature factors are listed in Table 1.§ Fig. 1 shows the bond lengths and bond angles in the molecule. The bond lengths and angles of the adenine moiety observed in the present study are in good agreement with those in the neutral adenine moieties (Voet & Rich, 1970) and kinetin (Soriano-Garcia & Parthasarathy, 1977). The bond angle C(6)—N(1)—C(2) = 118·2 (2)° and is in agreement with that reported for acetyladenosine [118·9 (3)°]. This is taken as a clear indication that N(1) is unprotonated (Rao & Sundaralingam, 1970). The bond angle N(3)—C(4)—C(5) = 126·1 (2)° and differs substantially (2°) from that observed in 2′-deoxy-2′-iminoadenosine [128·1 (4)°] (Rohrer & Sundaralingam, 1970) but it is in good agreement with that in two other neutral adenine bases: 3′-*O*-acetyladenosine (126·2°) (Rao & Sundaralingam, 1970) and deoxyadenosine (126·9°) (Watson, Suter & Tollin, 1965).

A view of the molecular packing down [100] is shown in Fig. 2. The molecule is unprotonated at its N(1) position which is proposed as a necessary condition for active cytokinins (Soriano-Garcia & Parthasarathy, 1975). The crystal exists as the N(9)—H tautomer as against the N(7)—H tautomeric form observed in N^6-benzoyladenine (Raghunathan & Pattabhi, 1981). This observation is further substantiated by the fact that C(8)—N(9) is 0·054 Å longer than

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§ Lists of structure factors, anisotropic thermal parameters, hydrogen-bond lengths and angles and details of least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38700 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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C(8)–N(7) and the angle C(8)–N(9)–C(4) is 2·5° larger than C(8)–N(7)–C(5). The N^6 substituent is distal to the imidazole ring as in the case of other active cytokinins. The torsion angles that describe the conformation of the molecule are compared with those of related structures in Table 2. The benzyl moiety is planar ($\chi^2 = 4{\cdot}8$) whereas the adenine ring deviates significantly from planarity ($\chi^2 = 266{\cdot}0$). The least-squares plane through the adenine ring is inclined approximately at right angles to the planes through the atoms of the side chain, the angle being 78·5 (3)°. This is comparable to those observed in other active cytokinins like kinetin (79°), N^6-(Δ^2-isopentenyl)-adenine (72°) (Bugg & Thewalt, 1972) and its 2-methyl thio analogue (91°) (McMullan & Sundaralingam, 1971).

Table 1. *Fractional positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters* (Å^2)

For non-hydrogen atoms $B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}$.

	x	y	z	B_{eq}/B_{iso}
N(1)	3399 (6)	2561 (3)	7845 (2)	4·2
N(3)	7393 (6)	4153 (3)	8851 (2)	4·1
N(6)	35 (6)	624 (3)	8408 (2)	3·9
N(7)	3442 (5)	1614 (3)	10388 (2)	3·8
N(9)	7429 (5)	3480 (3)	10507 (2)	4·0
C(2)	5769 (8)	3676 (4)	8028 (3)	4·6
C(4)	6335 (6)	3346 (4)	9574 (2)	3·5
C(5)	3869 (6)	2186 (4)	9498 (2)	3·5
C(6)	2396 (7)	1772 (4)	8584 (2)	3·7
C(8)	5616 (7)	2421 (4)	10963 (3)	4·2
C(10)	−1315 (8)	109 (5)	7428 (3)	4·2
C(11)	9 (7)	−1154 (4)	6818 (2)	3·9
C(12)	−202 (8)	−2736 (4)	7054 (3)	4·8
C(13)	1043 (10)	−3917 (6)	6523 (4)	6·7
C(14)	2523 (10)	−3493 (8)	5741 (4)	7·8
C(15)	2730 (12)	−1935 (9)	5498 (4)	8·3
C(16)	1495 (9)	−749 (7)	6043 (3)	5·9
H(N6)	81 (7)	986 (4)	110 (2)	2·0 (6)
H(N9)	906 (10)	425 (6)	83 (3)	3·9 (7)
H(C2)	360 (7)	584 (5)	252 (3)	1·8 (6)
H(C8)	599 (9)	231 (5)	168 (3)	4·2 (8)
H(C10)*A*	324 (7)	41 (4)	251 (2)	2·9 (6)
H(C10)*B*	127 (7)	886 (4)	286 (2)	3·2 (7)
H(C12)	129 (8)	301 (5)	237 (3)	4·2 (8)
H(C13)	919 (10)	507 (6)	329 (3)	6·2 (10)
H(C14)	656 (12)	435 (7)	461 (4)	9·0 (12)
H(C15)	372 (10)	848 (6)	500 (4)	5·7 (9)
H(C16)	831 (8)	962 (5)	413 (3)	5·0 (9)

Table 2. *Torsion angles* (°) *observed with the corresponding angles in other related structures*

	6BAN (present study)	N^6-(Δ^2-isopentenyl)-adenine	Kinetin* ribonucleoside	Kinetin
C(5)–C(6)–N(6)–C(10)	−174·4 (3)	−177·0 (1)	−168·0 (11)	174·2 (2)
C(6)–N(6)–C(10)–C(11)	80·9 (3)	92·2 (2)	73·6 (17)	−78·7 (3)
C(16)–C(11)–C(10)–N(6)	−110·0 (4)	−117·1 (1)	−120·6 (20)	107·8 (3)

* Walker & Tollin (1982).

The crystal packing seems to facilitate the linking of the bases across the crystallographic inversion centres by the N(9)–H···N(3) and N(6)–H···N(7) intermolecular hydrogen bonds using the Hoogsteen (1959) sites for base pairing. The hydrogen bonds link the molecules into zigzag ribbons along the *b* axis. This hydrogen-bonding pattern is observed in all active cytokinin structures so far solved, *viz* N^6-(Δ^2-isopentenyl)adenine and its 2-methyl thio analogue.

The N(9)···N(3) hydrogen-bond length is 2·935 (4) Å and N(6)···N(7) is 3·018 (4) Å. The N(9)–H···N(3) and the N(6)–H···N(7) angles are 166 (3) Å and 160 (2)° respectively, and the H···N(3) and H···N(7) distances are 1·976 (3) and 2·006 (3) Å.

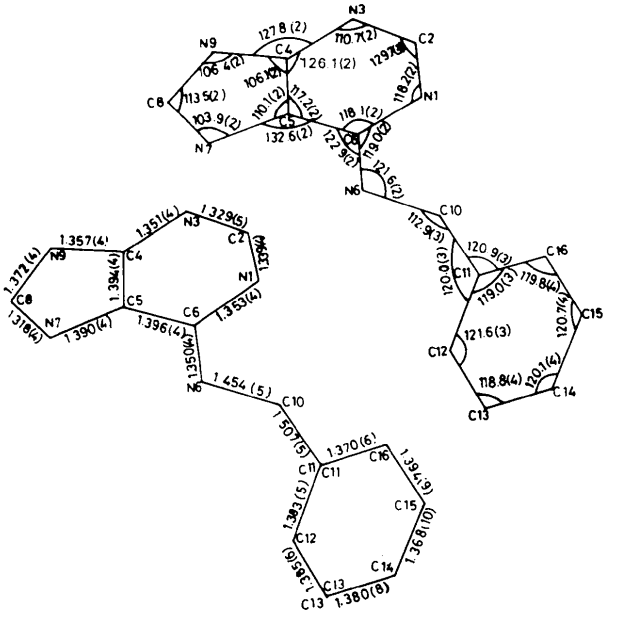

Fig. 1. Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses.

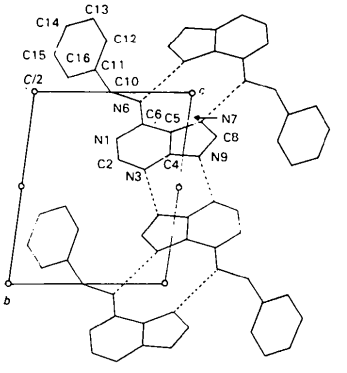

Fig. 2. Packing of the molecule down the *a* axis. Hydrogen bonds are indicated by broken lines.

There is only a slight overlap of bases, a situation similar to that found in the three other active cytokinins. Conformational features observed in this structure are in agreement with those observed for active cytokinins and are in disagreement with those in N^6-benzoyladenine which is reported to show mild cytokinin activity.

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Structure of 5-(4,5,6,7-Tetrahydrobenzimidazol-2-yl)valeronitrile, $C_{12}H_{17}N_3$

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Abstract. $M_r = 203{\cdot}29$, monoclinic, $P2_1/n$, $a = 9{\cdot}794$ (3), $b = 9{\cdot}044$ (4), $c = 26{\cdot}605$ (3) Å, $\beta = 97{\cdot}67$ (3)°, $V = 2335{\cdot}5$ Å^3, $Z = 8$, $D_m = 1{\cdot}16$, $D_x = 1{\cdot}157$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5405 Å, $\mu = 0{\cdot}56$ mm^{-1}, $F(000) = 880$, $T = 298$ K. Final $R = 0{\cdot}098$ for 2402 independent reflections. The aliphatic side chain of one molecule is statistically disordered over two sites and therefore three kinds of conformation of the side chains are observed: *trans–trans–gauche* with respect to the ring carbon for one molecule, and *gauche–trans–trans* and *gauche–trans–gauche* for the others. Both molecules are linked together by NH···N hydrogen bonds in strings of an infinite length along **a**.

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Introduction. In the reaction of 2-aminocyclohexanone oxime with ethyl acetimidate hydrochloride a new compound has been synthesized (Sato, Imamura & Kitano, 1983). The structure of the product was characterized by chemical and spectroscopic methods but could not be established exclusively. The compound, obtained in the form of single crystals, was then subjected to X-ray analysis and the structure was determined as 5-(4,5,6,7-tetrahydrobenzimidazol-2-yl)valeronitrile.

Experimental. Crystals grown from an ethyl acetate solution by slow evaporation at room temperature as