Fig. 3. The molecular packing and hydrogen bonding in the unit cell as viewed down the *b* axis.

molecular hydrogen-bonding pattern is similar to that observed for N^6-(2-isopentenyl)adenine (Bugg & Thewalt, 1972), in which N(1) is completely shielded, unlike the N(1) of 6-(2-phenethyl)purine.

A comparison of the crystal structure of the synthetic cytokinin (I) with those of the natural cytokinins, N^6-(2-isopentenyl)-2-methylthioadenine (McMullan & Sundaralingam, 1971a,b) and N^6-(2-isopentenyl)adenine (Bugg & Thewalt, 1972) indicates that in (I) neither H of the 6-CH_2 lies in the purine plane, as does the 6-NH. The side chain protrudes essentially straight out from C(6) in (I), whereas in N^6-monosubstituted adenines (Bugg & Sternglanz, 1974) the side chain is directed away from the imidazole ring of the base. Finally, the unsaturated portion of the side chain is nearly parallel to the purine ring in (I), in contrast to the dihedral angles of 91 and

72°, respectively, in the natural cytokinins in the order mentioned above. These comparisons indicate the latitude in side-chain conformation that is permitted for the expression of high cytokinin activity in substituted purines.

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Structure of 1-(2-Isopentenyl)adenine

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Abstract. $C_{10}H_{13}N_5$, $M_r = 203\cdot3$, monoclinic, $P2_1/c$, $a = 13\cdot577\,(4)$, $b = 6\cdot520\,(1)$, $c = 14\cdot546\,(4)$ Å, $\beta = 123\cdot97\,(2)°$, $V = 1068$ Å^3, $Z = 4$, $F(000) = 432$, $D_c = 1\cdot26$ Mg m^{-3}, $\mu(Mo\,K\alpha) = 0\cdot09$ mm^{-1}; $R = 0\cdot076$, $R_w = 0\cdot06$ for 1375 non-zero reflections. The tautomeric form in the crystal is 6-NH_2. The alkene side chain and the planar fused rings form a dihedral angle of 74°.

Introduction. 1-(2-Isopentenyl)adenine (I) (Leonard & Fujii, 1964) is of interest as a chemical precursor of the active cytokinin, N^6-(2-isopentenyl)adenine (Leonard, Achmatowicz, Loeppky, Carraway, Grimm, Szweykowska, Hamzi & Skoog, 1966). Determination

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of its structure would yield information concerning the preferred tautomeric form in the crystal, the orientation of the side chain with respect to the purine ring, and the intermolecular hydrogen-bonding pattern.

(I)
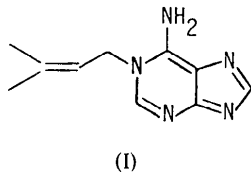
The title compound was recrystallized from ethanol, m.p. 510–512 K dec. Studies were carried out on a crystal of approximate dimensions $0.58 \times 0.30 \times 0.18$ mm. Cell dimensions were obtained by a least-squares fit to the settings for fifteen reflections (Mo $K\alpha$, $\lambda = 0.71069$ Å). Intensity data were collected on a Syntex $P2_1$ automated diffractometer (Mo $K\alpha$; graphite monochromator). Reflections in the range $2\theta = 1°$ to $50°$ were measured by a $\theta:2\theta$ scan with scan speeds ranging from 2 to $15°$ min^{-1}. The background to the scan time ratio used was 0.25. The intensities of three standard reflections, monitored every 57 reflections, showed no evidence of crystal deterioration during the data collection. Of the 3138 unique reflections collected over one quarter of the sphere, 1375 were considered non-zero at the 1σ level according to counting statistics. Lorentz and polarization corrections were applied to the data.

The weights were taken as $1/[\sigma(F_o)^2 + (0.02F_o)^2]$, where $\sigma(F_o)$ is the standard deviation based on counting statistics. The atomic scattering factors used in the calculation of all structure factors were taken from the analytical expressions given in *International Tables for X-ray Crystallography* (1974).

The structure was solved using the *MULTAN* series of programs (Germain, Main & Woolfson, 1971). The positions of most of the H atoms were obtained from a difference map and were reasonable. Full-matrix least-squares refinements on the positions and anisotropic thermal parameters of the non-hydrogen atoms and the positions of the H atoms converged to agreement factors $R = 0.076$ and $R_w = 0.06$.*† The final value of $[\sum w||F_o| - |F_c||^2/(m - n)]^{1/2}$, where m is the number of observations and n is the number of variables, was 1.53. A difference map, obtained after the last refinement of the model, contained no electron density peaks above 0.21 e Å^{-3}.

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* $R = \sum ||F_o| - |F_c||/\sum |F_o|$, $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$. The fixed isotropic thermal parameters assigned to the H atoms correspond to the last isotropic thermal parameters of the parent C atoms to which the H atoms are bonded.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35675 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
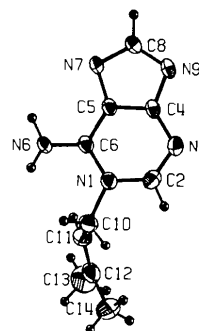

Fig. 1. View of a single molecule of $C_{10}H_{13}N_5$.

Table 1. *Final atomic coordinates for* (I) *in fractions of the unit-cell edge and equivalent isotropic thermal parameters for the heavy atoms*

	x	y	z	B_{eq} (Å^2)*
N(1)	0.1904 (2)	0.4782 (4)	0.1331 (2)	3.9 (1)
C(2)	0.2303 (3)	0.4198 (6)	0.2400 (3)	4.2 (1)
N(3)	0.2212 (2)	0.5221 (4)	0.3107 (2)	4.8 (1)
C(4)	0.1653 (2)	0.7054 (5)	0.2711 (2)	3.6 (1)
C(5)	0.1199 (2)	0.7760 (5)	0.1646 (2)	3.5 (1)
C(6)	0.1340 (2)	0.6610 (5)	0.0915 (2)	3.7 (1)
N(6)	0.0957 (3)	0.7211 (5)	−0.0098 (2)	5.0 (1)
N(7)	0.0700 (2)	0.9651 (4)	0.1507 (2)	4.4 (1)
C(8)	0.0895 (3)	0.9961 (6)	0.2504 (3)	4.3 (2)
N(9)	0.1459 (2)	0.8485 (4)	0.3267 (2)	4.2 (1)
C(10)	0.2113 (3)	0.3358 (6)	0.0660 (3)	5.0 (2)
C(11)	0.3243 (3)	0.3760 (6)	0.0780 (3)	5.5 (2)
C(12)	0.4056 (3)	0.2395 (7)	0.0979 (3)	6.6 (2)
C(13)	0.5174 (6)	0.3064 (13)	0.1096 (6)	11.5 (4)
C(14)	0.3946 (6)	0.0185 (10)	0.1080 (5)	9.4 (3)
H(2)	0.270 (2)	0.295 (4)	0.260 (2)	
H(6)	0.122 (2)	0.664 (4)	−0.048 (2)	
H(6')	0.055 (2)	0.845 (4)	−0.031 (2)	
H(8)	0.066 (2)	1.122 (4)	0.265 (2)	
H(10A)	0.204 (2)	0.186 (5)	0.086 (2)	
H(10B)	0.143 (3)	0.347 (4)	−0.006 (2)	
H(11)	0.344 (3)	0.511 (4)	0.077 (2)	
H(13A)	0.523 (4)	0.453 (7)	0.096 (4)	
H(13B)	0.575 (4)	0.240 (7)	0.172 (4)	
H(13C)	0.516 (4)	0.238 (7)	0.049 (4)	
H(14A)	0.333 (4)	−0.016 (7)	0.127 (4)	
H(14B)	0.460 (4)	−0.039 (7)	0.167 (4)	
H(14C)	0.357 (4)	−0.066 (7)	0.043 (4)	

* $B_{eq} = \frac{4}{3}\sum_i \sum_j \beta_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)$.

Discussion. A view of the molecule of 1-(2-isopentenyl)adenine, together with the atom numbering used in the analysis, is given in Fig. 1. Listed in Table 1 are the final atomic coordinates, and in Table 2 the bond lengths and bond angles for (I). The molecule exhibits a planar fused-ring skeleton with the plane of the side-chain atoms C(10)—C(14) (Fig. 1) inclined 74° with respect to the purine plane. This is close to the dihedral angle, 72°, observed between the isopentenyl side chain and the purine plane in N^6-(2-isopenten-

Table 2. *Bond lengths* (Å) *and angles* (°)

N(1)—C(2)	1·385 (4)	C(5)—N(7)	1·366 (4)
N(1)—C(6)	1·362 (4)	C(6)—N(6)	1·319 (4)
N(1)—C(10)	1·484 (5)	N(7)—C(8)	1·336 (4)
C(2)—N(3)	1·287 (5)	C(8)—N(9)	1·340 (4)
N(3)—C(4)	1·359 (4)	C(10)—C(11)	1·468 (7)
C(4)—C(5)	1·387 (4)	C(11)—C(12)	1·318 (7)
C(4)—N(9)	1·353 (4)	C(12)—C(13)	1·494 (11)
C(5)—C(6)	1·399 (4)	C(12)—C(14)	1·465 (8)

C(2)—N(1)—C(6)	120·6 (3)	N(6)—C(6)—N(1)	122·0 (3)
C(2)—N(1)—C(10)	117·9 (3)	N(6)—C(6)—C(5)	123·6 (3)
C(6)—N(1)—C(10)	121·5 (3)	N(1)—C(6)—C(5)	114·4 (3)
N(3)—C(2)—N(1)	127·1 (4)	C(8)—N(7)—C(5)	101·2 (3)
C(4)—N(3)—C(2)	113·4 (3)	N(9)—C(8)—N(7)	117·8 (3)
C(5)—C(4)—N(9)	109·0 (3)	C(4)—N(9)—C(8)	102·2 (3)
C(5)—C(4)—N(3)	124·0 (3)	C(11)—C(10)—N(1)	112·4 (3)
N(9)—C(4)—N(3)	127·0 (3)	C(12)—C(11)—C(10)	126·7 (4)
C(6)—C(5)—N(7)	129·7 (3)	C(13)—C(12)—C(14)	115·5 (5)
C(6)—C(5)—C(4)	120·4 (3)	C(13)—C(12)—C(11)	120·0 (5)
N(7)—C(5)—C(4)	109·8 (3)	C(14)—C(12)—C(11)	124·5 (5)

Fig. 2. A stereoview of the packing of (I).

yl)adenine (Bugg & Thewalt, 1972) and may be compared with the corresponding values of 91° (89°) in N^6-(2-isopentenyl)-2-methylthioadenine (McMullan & Sundaralingam, 1971*a,b*) and 104° (76°) in 3-(2-isopentenyl)adenine (Kistenmacher, Urmey & Rossi, 1977), also known as triacanthine (Leonard & Deyrup, 1962). The amine group in (I) is twisted out of the plane of the fused rings by 16·5 (2)°. The values for the C=N bond lengths (Table 2) show less deviation from the average in (I) than the C=N bond lengths in the N^6-alkenyladenines, suggesting that the original aromatic representation of 1-(2-isopentenyl)adenine (Leonard & Fujii, 1964) was presciently correct. The C—H bond lengths were in the range 0·90–1·04 (6) Å and the N—H in the range 0·89–0·93 (3) Å.

The fact that (I) is clearly in the 6-NH_2 tautomeric form in the crystal is indicative of probable generality for related 1-substituted adenines. As determined by spectroscopy, in aqueous solution the amino form of 1-alkyladenines predominates (Dreyfus, Dodin, Bensaude & Dubois, 1977; Leonard, Carraway & Helgeson, 1965), as it does in dimethyl sulfoxide solution (Townsend, 1973), and the mechanism of the amino ⇌ imino (9*H*) interconversion has been examined by temperature-jump relaxation in D_2O solution. The 9*H* and 7*H* imino forms of 1-alkyladenines predominate in a nonpolar environment (Dreyfus *et al.*, 1977). 3-Substituted adenines, which exist in the 6-NH_2 form in the crystal (Kistenmacher *et al.*, 1977; Petersen & Furberg, 1975), exist also in the amino form in both polar and nonpolar media (Kistenmacher *et al.*, 1977; Leonard & Deyrup, 1962). The exocyclic bond length C(6)—N(6) is shorter in 1-(2-isopentenyl)adenine (I), 1·319 (4) Å, than in 3-(2-isopentenyl)adenine, 1·327 (3) Å, and in 3-ethyladenine, 1·330 (3) Å.

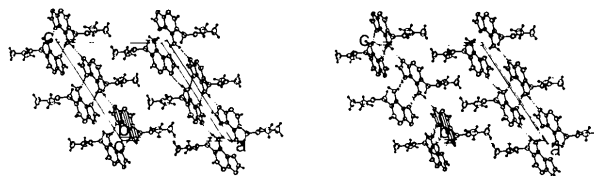The molecules of (I) are held together in a three-dimensional network of hydrogen bonds (Fig. 2). The inversion-related pairs are held together through N(6)—H(6′)···N(7) [N(6)—H(6′) 0·93, H(6′)···N(7) 2·04 Å, ∠N(6)—H(6′)···N(7) 151 (3)°] and these pairs are then linked to the glide-related molecules through N(9)···H(6)—N(6) [N(9)···H(6) 2·02, H(6)—N(6) 0·89 Å, ∠N(9)···H(6)—N(6) 154 (3)°]. The out-of-plane NH_2 twist (16·5°) appears to maximize the intermolecular hydrogen bonding. Seperate layers of side chains and heterocyclic nuclei are observed. The closest stacking distance that the purine layers make with each other (purine at x, y, z and $-x, 1 - y, -z$) is 3·445 Å, a typical distance for such systems. As with N^6-(2-isopentenyl)adenine, there is very little overlap of the ring systems (Bugg & Thewalt, 1972).

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