4·138 (7) Å and the Te···Te···Te angles 73·4 (1) and 72·9 (1)°. If the C(8) methyl group were axially substituted on C(3), then disruption of the Te···Te associations would be expected as a result of forcing the molecules further apart in the *b* direction, and it is noteworthy that in (*A*), where the central C atom has two methyl substituents, the closest Te···Te distance is 5·05 Å and no Te polymer is found.

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Stereochemistry and Hydrogen Bonding of Cytokinins: 6-Furfurylaminopurine (Kinetin)

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Abstract. $C_{10}H_9N_5O$, triclinic, space group $P\bar{1}$, with (at 22 ± 3 °C) a = 7·874 (3), b = 12·526 (3), c = 4·947 (1) Å, α = 91·15 (4), β = 99·15 (6), γ = 96·35 (4)°, D_o = 1·49, D_c = 1·50 g cm^{-3}, Z = 2, μ(Cu $K\alpha$) = 8·9 cm^{-1} [λ(Cu $K\alpha_1$) = 1·54051 Å]. The structure was refined to an R index of 0·06 by the least-squares method using the block-diagonal approximation. The orientation of the N(6) substituent, distal to the imidazole ring of the adenine base, prevents the Watson–Crick sites from hydrogen bonding. The molecules in the crystal exist in the N(9)–H tautomeric form and are linked across centers of inversion by pairs of N(6)–H···N(7) and N(9)–H···N(3) hydrogen bonds forming continuous ribbons. This mode of hydrogen bonding and packing is observed also for two other cytokinins, isopentenyladenine and its 2-methylthio derivative.

Introduction. Kinetin is a highly potent growth factor (cytokinin). Cytokinin is the generic name used to designate plant-growth substances that play a major role in cell division and cell differentiation (Helgeson, 1968; Skoog & Armstrong, 1970; Hall, 1973). The occurrence of cytokinin activity has been limited mainly to 6-substituted purine derivatives, but there are exceptions (Hall, 1973; see also Tovigoe, Akiyama, Hirobe, Okamoto & Isogai, 1971). Kinetin is used as a reference compound for comparing cytokinin activities of other cytokinins and for deducing structure–activity relationships of these compounds. As part of a continuing program of research in our laboratory on the stereochemistry of the cytokinin compounds, we have now determined and present here the three-dimensional structure and conformation of kinetin. The structure–activity relationships of cytokinins have been discussed by us earlier (Soriano-Garcia & Parthasarathy, 1975).

Suitable crystals of kinetin (6-furfurylaminopurine) (Sigma Chemical Co.) for X-ray work were obtained by slow cooling of a hot ethanol solution. The resulting

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crystals were colorless, transparent and in the shape of thin plates. The unit-cell parameters (see *Abstract*) were determined by a least-squares refinement of the 2θ values of 60 reflections measured on a diffractometer. A crystal, 0·26 × 0·30 × 0·35 mm, was chosen for the X-ray analysis and mounted on a glass fiber with **b*** along the φ axis of the goniostat. 2213 reflections (to the limit $2\theta = 160°$ for Cu $K\alpha$) were collected on a GE XRD5 diffractometer equipped with Ross filters, by the stationary-crystal stationary-counter technique (Furnas & Harker, 1955) using a 5° take-off angle. Of these, 2120 reflections had intensities at least twice the average background intensity. Four reflections were periodically monitored during the intensity-collection period. The intensities were converted to their corresponding structure amplitudes by applying Lorentz, polarization, and $\alpha_1 - \alpha_2$-splitting corrections.

A partial solution of the structure was obtained by the application of the multisolution tangent refinement technique, employing the program *MULTAN* of Germain, Main & Woolfson (1971). An E map calculated from the solution with the highest figure of merit (1·1812) yielded a partial structure containing only the nine atoms corresponding to the adenine moiety. A structure factor calculation for this partial structure gave an R value of 0·46. Attempts to refine this structure in $P\bar{1}$ by the least-squares method and to locate the remaining parts of the molecule from difference maps were not fruitful. We recognized that this difficulty may have been due to: (*a*) the space group being $P1$ with the two molecules adopting slightly different conformations for the side chains, or (*b*) the molecules in $P\bar{1}$ not being correctly placed with respect to the center of inversion. The molecules in $P\bar{1}$ can be correctly placed with respect to the origin by using the translation functions suggested by Karle (1972) or more simply by calculating the ring–ring vector distance from a Patterson map and comparing it with the distance obtained for the observed fragments; still, this procedure will not determine whether the space group is $P1$ or $P\bar{1}$. We thought that a simple refinement in $P1$ might move the two molecules to the correct relative positions and also indicate the locations of the remaining atoms by means of improved phases, despite the known ambiguity in such a procedure (Parthasarathy, Sime & Speakman, 1969). Our expectations were fulfilled; with refinement in $P1$ the molecule shifted, the average shift being 0·54, 0·15 and 0·51 Å along the a, b and c axes respectively. The refinement in $P1$ with individual isotropic thermal parameters led to an R of 0·16. Since the two molecules appeared to have almost identical conformations, the space group was changed to $P\bar{1}$ with the origin midway between the molecules; continuation of the refinement in $P1$ would have given ambiguities of the type discussed in Parthasarathy, Sime & Speakman (1969). Further refinement, including individual anisotropic temperature factors (blocks of 9 × 9) for the non-hydrogen atoms, reduced R to 0·10. A difference electron density map calculated at this stage indicated the positions of the nine H atoms. A few cycles of refinement with anisotropic parameters for the non-hydrogen atoms and isotropic parameters for the H atoms resulted in an R of 0·06. Refinement at this point was terminated when the corresponding shifts for the non-hydrogen atoms were of the order of 0·1 (and for the H atoms, 0·3) of the corresponding e.s.d.'s. The function minimized was $\Sigma w(|F_o| - 1/k|F_c|)^2$ with $w = 1/f_C^2$, f_C being the scattering factor for the C atom. This weighting results in a flat $\Sigma w\Delta^2$ *versus* $(\sin\theta/\lambda)$ plot for the stationary-crystal stationary-counter data. The atomic scattering factors for O, N and C and the corresponding anomalous dispersion correction factors were those given by Cromer & Liberman (1970). For H, the scattering factors of Stewart, Davidson & Simpson (1965) were used. The final atomic parameters* and their e.s.d.'s as obtained from the inverse of the block-diagonal matrix are listed in Tables 1 and 2.

Table 1. *Final fractional atomic coordinates* (×10⁴) *for heavy atoms*

	x	*y*	*z*
O(15)	2902 (3)	3157 (2)	4715 (5)
N(1)	−2568 (3)	2379 (2)	1120 (5)
N(3)	−4156 (3)	1246 (2)	−2662 (5)
N(6)	−564 (3)	1754 (2)	4557 (5)
N(7)	−1583 (3)	−436 (2)	1648 (5)
N(9)	−3440 (3)	−594 (2)	−2326 (5)
C(2)	−3699 (4)	2177 (2)	−1202 (6)
C(4)	−3334 (3)	463 (2)	−1459 (5)
C(5)	−2157 (3)	534 (2)	991 (5)
C(6)	−1752 (3)	1571 (2)	2262 (5)
C(8)	−2402 (4)	−1079 (2)	−421 (6)
C(10)	−31 (4)	2846 (2)	5723 (6)
C(11)	1271 (4)	3463 (2)	4336 (6)
C(12)	1196 (5)	4270 (3)	2648 (8)
C(13)	2837 (6)	4491 (3)	1866 (9)
C(14)	3824 (5)	3805 (3)	3180 (9)

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32620 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Final fractional atomic coordinates* (×10³) *for* H *atoms*

	x	*y*	*z*
H(N6)	−7 (3)	120 (2)	535 (5)
H(N9)	−416 (4)	−80 (3)	−383 (7)
H(C2)	−429 (3)	273 (2)	−200 (5)
H(C8)	−218 (4)	−182 (2)	−40 (7)
H(C10*a*)	36 (4)	274 (2)	765 (6)
H(C10*b*)	−101 (4)	324 (3)	581 (7)
H(C12)	35 (5)	456 (3)	197 (7)
H(C13)	320 (5)	495 (3)	57 (8)
H(C14)	487 (5)	369 (3)	293 (8)

Discussion. Figs. 1 and 2 illustrate the interatomic distances and angles of the kinetin molecule. The bond angles and distances of the adenine moiety are in good agreement with the corresponding values found for neutral adenine (for a review, see Voet & Rich, 1970). The C(6)–N(6) bond is slightly longer in this structure than in unsubstituted adenine and derivatives. This tendency in N(6)-substituted adenines has been pointed out earlier (Parthasarathy, Ohrt & Chheda, 1974*a*). The bond lengths of the furan ring in kinetin show reasonable agreement with the values in *trans*-β-2-furylacrylamide (Leiserowitz & Rabinovich, 1969) and *trans*-β-2-furylacrylic acid (Filippakis & Schmidt, 1967). The exocyclic angles C(10)–C(11)–C(12) and C(10)–C(11)–O(15) differ by more than 16° in all three structures. This difference is also observed in 3,4-furandicarboxylic acid (Williams & Rundle, 1964) and 2,5-furandicarboxylic acid (Martuscelli & Pedone, 1968).

The conformation of the kinetin molecule [the distal conformation of the N(6) substituent] (Parthasarathy, Ohrt & Chheda, 1974*a*,*b*) and a comparison with conformations of other cytokinins, and the relation of molecular conformation to activity, have been discussed elsewhere (Soriano-Garcia & Parthasarathy, 1975).

Fig. 3 shows the hydrogen-bonding scheme. Since the N(6) substituent is distal to the imidazole ring, hydrogen bonding involving the Watson–Crick (1953) sites is not possible here. Two adenine moieties are self-paired across the center of inversion at $(0,0,\frac{1}{2})$ by a pair of N(6)–H(N6)···N(7) hydrogen bonds using the Hoogsteen (1959) sites in base pairing. There is also another specific self-pairing of two adenines across the center at $(\frac{1}{2},0,\frac{1}{2})$ by a pair of N(9)–H(N9)···N(3) hydrogen bonds. This pairing of the bases across centers of inversion results in continuous ribbons of purine bases along the *a* axis with the furfuryl rings pointing up and down from these sheets. It is very remarkable that the three cytokinins, kinetin, isopentenyladenine (Bugg & Thewalt, 1972) and its 2-methylthio derivative (McMullan & Sundaralingam, 1971), possess similarities not only in conformation

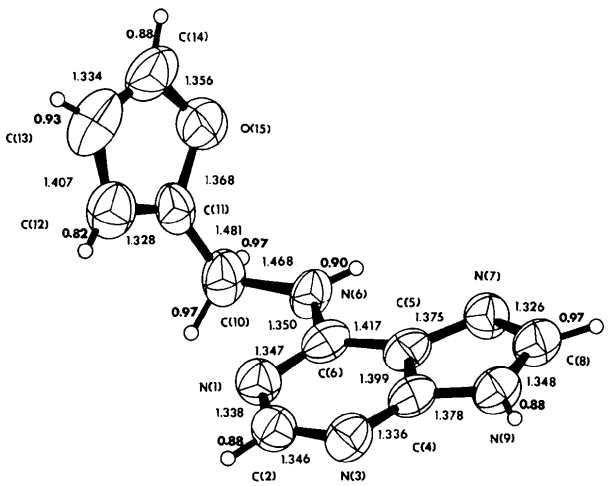

Fig. 1. Valence bond lengths (Å). The average estimated standard deviation is 0·004 Å in bond lengths. All the figures were drawn with *ORTEP* (Johnson, 1965).

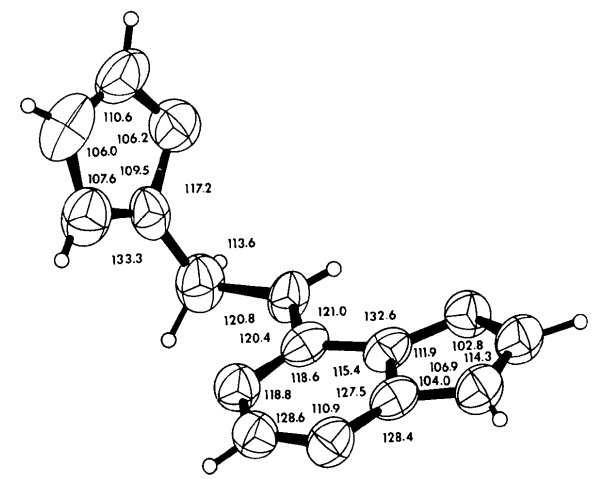

Fig. 2. Valence bond angles (°) excluding those involving H atoms. The average estimated standard deviation is 0·3° in bond angles.

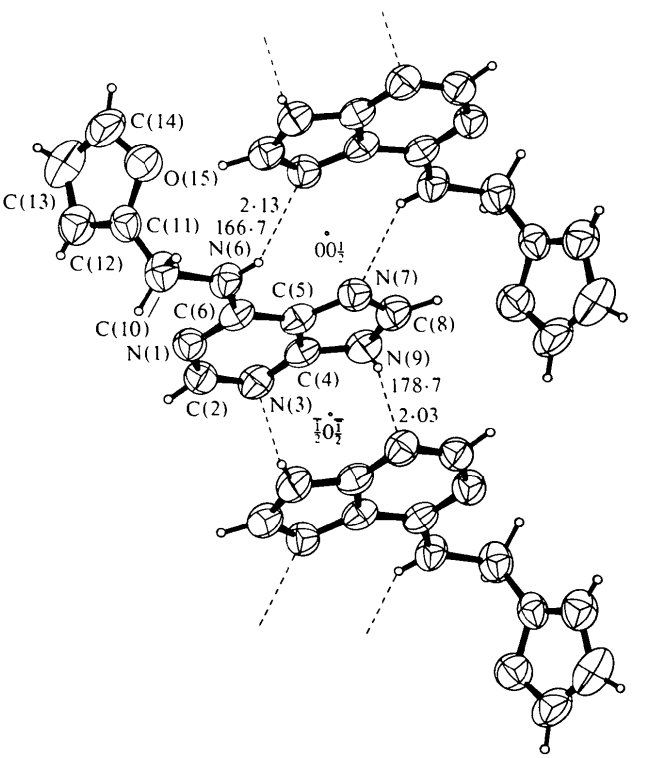

Fig. 3. The ribbon of hydrogen-bonded molecules viewed down **c**.

(Soriano-Garcia & Parthasarathy, 1975) but also in hydrogen bonding; indeed, they even crystallize in the same space group, $P\bar{1}$. Since the adenylcytokinins are all N(6)-substituted and since they all are expected to have similar conformations (Soriano-Garcia & Parthasarathy, 1975), it is possible that the specific hydrogen bonding seen in these three cytokinins may be a general structural feature of this class of compounds. This pattern of hydrogen bonding is not possible for the ribonucleosides of the cytokinin bases [as 6-benzyladenosine (Takeda, Ohashi, Sasada & Kakudo, 1976)] nor for the N(7)—H tautomers. In histaminopurine (not a cytokinin) (Thewalt & Bugg, 1972), the presence of the N(7)—H tautomer completely alters the hydrogen-bonding pattern. The N(7)—H and N(6)—H of one molecule are hydrogen bonded to N(3) and N(9) (both acceptors) respectively, of another molecule. There is no symmetrical interchange of the hydrogen bonds (as in self-pairing) and hence the hydrogen-bonding pairs cannot relate molecules across centers of inversion.

In addition to the hydrogen bonds mentioned above, there are two weak C—H···O contacts. The C(8)—H(C8)···O(15) contact [H(C8)···O(15), 2·64 Å, C—H···O, 124°] is between molecules related by the use of Hoogsteen sites. The C(2)—H(C2)···O(15) contact [H(C2)···O(15), 2·64 Å, C—H···O, 143·8°] is between the reference molecules and another related by the symmetry $-1 + x, y, -1 + z$.

There is hardly any stacking of the bases in kinetin, a situation very similar to that in the other two cytokinins.

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