

Table 4. Bond angles (°)

C(4)—N(1)—C(1)	112.6 (1)	C(2)—C(1)—N(1)	107.0 (2)
O(11)—C(1)—N(1)	127.1 (2)	O(11)—C(1)—C(2)	125.9 (2)
C(3)—C(2)—C(1)	108.5 (2)	C(21)—C(2)—C(1)	121.0 (2)
C(21)—C(2)—C(3)	130.5 (2)	C(4)—C(3)—C(2)	110.2 (2)
C(31)—C(3)—C(2)	127.8 (2)	C(31)—C(3)—C(4)	122.0 (2)
C(3)—C(4)—N(1)	101.7 (1)	C(5)—C(4)—N(1)	112.9 (1)
C(5)—C(4)—C(3)	111.9 (2)	C(6)—C(5)—C(4)	116.9 (2)
C(9)—N(6)—C(6)	109.4 (1)	N(6)—C(6)—C(5)	123.2 (2)
C(7)—C(6)—C(5)	128.3 (2)	C(7)—C(6)—N(6)	108.2 (2)
C(8)—C(7)—C(6)	107.4 (2)	C(71)—C(7)—C(6)	126.3 (2)
C(71)—C(7)—C(8)	126.3 (2)	C(9)—C(8)—C(7)	107.1 (2)
C(81)—C(8)—C(7)	125.4 (2)	C(81)—C(8)—C(9)	127.4 (2)
C(8)—C(9)—N(6)	108.0 (2)	C(91)—C(9)—N(6)	119.0 (2)
C(91)—C(9)—C(8)	133.0 (2)	C(32)—C(31)—C(3)	113.1 (2)
C(82)—C(81)—C(8)	110.8 (2)	C(83)—C(82)—C(81)	112.8 (2)
O(83)—C(83)—C(82)	125.1 (2)	O(84)—C(83)—C(82)	112.8 (2)
O(84)—C(83)—O(83)	122.0 (2)	C(85)—O(84)—C(83)	116.4 (2)
O(91)—C(91)—C(9)	111.8 (2)	O(92)—C(91)—C(9)	124.9 (2)
O(92)—C(91)—O(91)	123.3 (2)	C(93)—O(91)—C(91)	121.4 (1)
C(94)—C(93)—O(91)	101.4 (2)	C(95)—C(93)—O(91)	109.9 (2)
C(95)—C(93)—C(94)	112.2 (3)	C(96)—C(93)—O(91)	110.5 (2)
C(96)—C(93)—C(94)	110.0 (2)	C(69)—C(93)—C(95)	112.2 (2)

The interplanar angle in (1) is 99.6°. This is similar to those of 98 and 107° between the methylene-bridged ring systems in bilirubin (Bonnert, Davies & Hursthouse, 1976) and in a biladiene-*ac* dihydrobromide derivative (Struckmeier, Thewalt & Engel, 1976) respectively. An angle of 71.9° has been observed for a model 2,2'-methylendipyrrole (Bonnert, Hursthouse & Neidle, 1972). In bilirubin six intra-

molecular N—H...O hydrogen bonds stabilize this arrangement. In (1) the molecules are linked together through linear intermolecular N(1)—H(11)...O(92) and N(6)—H(61)...O(11) hydrogen bonds of 2.86 and 2.85 Å respectively. The C(91)—O(92) carbonyl group is *syn* to the N(6)—H(61) vector. Surprisingly it is twisted somewhat out of the plane of the pyrrole ring [C(91) 0.039, O(92) 0.235, O(91) -0.192 Å from this plane], presumably as a result of steric contacts between O(91) and C(81) and C(82) [O(91)...C(81) 2.95, O(91)...C(82) 3.34 Å].

We are indebted to Frau A. Borkenstein for technical assistance.

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4-Methylheptane-3,5-dionato(2-)-C²,C⁶-tellurium(II)*

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Abstract. C₈H₁₂O₂Te, monoclinic, *P*2₁, *a* = 8.80 (1), *b* = 4.92 (1), *c* = 11.04 (2) Å, β = 93.3 (1)°, *M_r* = 267.8, *U* = 477.2 Å³, *Z* = 2, *D_m* = 1.87, *D_c* = 1.86 g cm⁻³, *F*(000) = 256. Mo *K*α radiation (λ = 0.7107 Å;

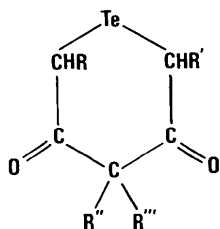
μ = 28.5 cm⁻¹). The structure was solved by the heavy-atom method from 789 two-circle diffractometer reflexions and refined by full-matrix least squares to *R* 0.048. In the molecules of the compound each Te^{II} atom is bonded to one bivalent 'bidentate chelate ligand' *via* the C² and C⁶ carbon atoms [Te—C 2.18 (1) Å; C—Te—C 89.3 (6)°] forming a heterocyclic ring of chair conformation with the three methyl substituents all in equatorial positions.

* Studies on Tellurium–Carbon Bonded Compounds. IV. Part III: Dewan & Silver (1977c).

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Introduction. We have previously reported the crystal structures of compounds *A*, *B*, *C*, and *D*.



- (A): $R = R' = \text{H}; R'' = R''' = \text{CH}_3$, (Dewan & Silver, 1976, 1977a)
 (B): $R = R' = \text{CH}_3; R'' = R''' = \text{H}$ (Dewan & Silver, 1977b)
 (C): $R = R' = R'' = R''' = \text{H}$ (Dewan & Silver, 1977c)
 (D): $R = R'' = \text{CH}_3; R' = R''' = \text{H}$ (Dewan & Silver, 1977d)
 (E): $R = R' = R'' = \text{CH}_3; R''' = \text{H}$ (This study)

Crystals of the present compound (E) were obtained from the museum in the Chemistry Department of this University and were prepared by Morgan & Drew (1925). (E) is isomorphous and pseudo-isostructural with the previously determined (B) (Dewan & Silver, 1977b), and the details of their data collection and structure determination are the same, except that for (E) anisotropic thermal parameters were only refined

Table 1. Fractional atomic coordinates ($\times 10^5$ for Te, $\times 10^4$ for C and O, $\times 10^3$ for H) and thermal parameters, with estimated standard deviations in parentheses

U was fixed at 0.05 \AA^2 for all H atoms.

	x	y	z	U ($\text{\AA}^2 \times 10^3$)
Te	13908 (9)	0*	10870 (8)	‡
C(1)	-25 (12)	29 (71)	2647 (10)	41 (3)
C(2)	950 (14)	-1747 (33)	3611 (11)	34 (3)
C(3)	2362 (11)	-161 (53)	4144 (9)	32 (3)
C(4)	3538 (10)	43 (50)	3175 (8)	29 (2)
C(5)	3200 (15)	1969 (33)	2190 (12)	41 (3)
C(6)	4526 (16)	2626 (41)	1437 (15)	55 (4)
C(7)	-1518 (17)	-1680 (41)	2287 (14)	53 (4)
C(8)	3029 (15)	-1714 (36)	5304 (12)	40 (3)
O(1)	627 (11)	-4079 (22)	3924 (9)	57 (3)
O(2)	4689 (10)	-1453 (23)	3226 (8)	42 (2)
H(11)*	-8	216	299	
H(32)*	134	147	416	
H(51)*	231	368	260	
H(61)†	495 (2)	83 (4)	101 (2)	
H(62)†	544 (2)	357 (4)	198 (2)	
H(63)†	410 (2)	404 (4)	75 (2)	
H(71)†	-201 (2)	-69 (4)	148 (1)	
H(72)†	-228 (2)	-147 (4)	301 (1)	
H(73)†	-135 (2)	-381 (4)	210 (1)	
H(81)†	221 (2)	-178 (4)	600 (1)	
H(82)†	407 (2)	-77 (4)	567 (1)	
H(83)†	327 (2)	-376 (4)	501 (1)	

* Parameters not refined.

† Refined as rigid groups pivoting on C(6), C(7), and C(8).

‡ Anisotropic thermal parameters ($\text{\AA}^2 \times 10^4$) for Te are in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^* + \dots)]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Te	492 (5)	486 (6)	472 (5)	165 (10)	-76 (3)	-75 (11)

for the Te atom. The weighting scheme employed in the final stages of refinement was $w = [\sigma^2(F_o) + (0.02|F_o|^2)]^{-1}$, the final R being 0.048 and $R' = \{[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}\} = 0.053$ for the preferred hand.* Parameters determined are listed in Tables 1–3; Fig. 1 shows a projection of the unit cell.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32617 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Interatomic distances (\AA) and angles ($^\circ$) with estimated standard deviations in parentheses

Values for rigid groups are not listed.

Te...Te ⁱ	4.138 (7)	C(3)–H(32)	1.21
Te–C(1)	2.18 (1)	C(4)–C(5)	1.46 (2)
Te–C(5)	2.18 (1)	C(4)–O(2)	1.25 (1)
C(1)–C(2)	1.59 (3)	C(5)–C(6)	1.51 (2)
C(1)–C(7)	1.59 (3)	C(5)–H(51)	1.25
C(1)–H(11)	1.12	C(2)...O(1 ^{iv})	3.39 (2)
C(2)–C(3)	1.55 (2)	C(8)...O(2 ⁱⁱⁱ)	3.42 (2)
C(2)–O(1)	1.24 (2)	C(3)...O(1 ^{iv})	3.36 (3)
C(3)–C(4)	1.53 (1)	C(1)...O(1 ^{iv})	3.26 (3)
C(3)–C(8)	1.58 (2)	H(11)...O(1 ^{iv})	2.19
Te ⁱ –Te–Te ^v	72.9 (1)	C(2)–C(3)–H(32)	76
C(1)–Te–C(5)	89.3 (6)	C(4)–C(3)–C(8)	111 (1)
Te–C(1)–C(2)	102.4 (9)	C(4)–C(3)–H(32)	120
Te–C(1)–C(7)	107 (1)	C(8)–C(3)–H(32)	124
Te–C(1)–H(11)	108	C(3)–C(4)–C(5)	116 (1)
C(2)–C(1)–C(7)	106 (2)	C(3)–C(4)–O(2)	120 (1)
C(2)–C(1)–H(11)	109	C(5)–C(4)–O(2)	123 (1)
C(7)–C(1)–H(11)	122	C(4)–C(5)–Te	103.8 (9)
C(1)–C(2)–C(3)	112 (2)	C(4)–C(5)–C(6)	115 (1)
C(1)–C(2)–O(1)	125 (1)	C(4)–C(5)–H(51)	106
C(3)–C(2)–O(1)	124 (1)	C(6)–C(5)–Te	111 (1)
C(2)–C(3)–C(4)	109 (1)	C(6)–C(5)–H(51)	125
C(2)–C(3)–C(8)	108 (2)	Te–C(5)–H(51)	92

Symmetry code

- (i) $-x, \frac{1}{2} + y, -z$ (iv) $x, 1 + y, z$
 (ii) $-x, \frac{1}{2} + y, 1 - z$ (v) $-x, -\frac{1}{2} + y, -z$
 (iii) $1 - x, -\frac{1}{2} + y, 1 - z$

Table 3. Deviations (\AA) of atoms from the least-squares plane through C(1), C(2), C(4), C(5)

The equation of the plane is $-1.12x + 3.57y + 7.54z = 2.00$, where x, y, z are the fractional coordinates of the defining atoms in the direct cell.

Te	-1.34	C(7)	-0.71
C(1)	0.01	C(8)	1.05
C(2)	-0.01	O(1)	-0.57
C(3)	0.80	O(2)	-0.61
C(4)	0.01	H(11)	1.03
C(5)	-0.01	H(32)	1.51
C(6)	-0.49	H(51)	1.01

Discussion. The structure consists of molecules of the compound arranged in a zigzag polymeric manner about the 2_1 axes at $x = 0$ and $z = 0$ (Fig. 1). This structure is isomorphous and pseudo-isomorphous with (*B*) (Dewan & Silver, 1977*b*), the only difference between the molecules being the substitution of H(31) in (*B*) for an equatorial methyl group [C(8), H(81)–H(83)] on C(3); the atomic-numbering scheme used here is thus the same as for (*B*), apart from this difference.

The mode of attachment displayed by the β -diketone in the present structure, and in those of (*A*)–(*D*), represents a deviation from the usual modes of attachment of pentane-2,4-dione, and its derivatives, where bonding usually occurs through the O atoms or central C atom (Dewan & Silver, 1977*d*). The Te atom has a formal oxidation state of +2 and the 'ligand' is therefore bivalent. The Te^{II} atom bonds to C(1) and C(5) at distances of 2.18 (1) Å and these distances are the same, within experimental error, as those found in (*A*)–(*D*). The C–O carbonyl distances [1.24 (2) and 1.25 (1) Å] are typical of a ketonic carbonyl. The six-membered heterocyclic ring of the compound has the chair conformation (Table 3), and again this is in agreement with (*A*)–(*D*). The three methyl substituents on the ring are all in equatorial positions.

The closest intermolecular non-hydrogen atom contacts of the structure are given in Table 2. That involving the carbonyl C(2) [C(2)⋯O(1ⁱⁱ) 3.39 (2) Å]

must represent a non-bonding contact, while C(1)⋯O(1^{iv}), C(3)⋯O(1^{iv}), and C(8)⋯O(2ⁱⁱⁱ) [3.26 (3), 3.36 (3) and 3.42 (2) Å] are all rather long to be considered hydrogen-bonding interactions (Hamilton & Ibers, 1968).

Donaldson, Laughlin, Ross & Silver (1973), Donaldson & Silver (1974, 1976), and Donaldson, Silver, Hadjiminolis & Ross (1975) have suggested that the colours of *p*-block materials can be explained in terms of the donation of non-bonding valence electron density into bands formed by the overlap of empty *p* or *d* orbitals on the ligands or on the electron-donating atoms themselves. If the sp^2 -hybridization scheme is used for the Te atom (Dewan & Silver, 1977*d*), the *p* orbital on each Te^{II} atom will lie approximately along **b**, and these are then aligned (together with empty Te 5*d* orbitals) so that a weak overall bonding orbital is then possible between them. These weak associations could then account for the bright yellow colour of the compound.

In the present structure, the Te⋯Te distance [4.138 (7) Å] is similar to those in (*B*)–(*D*) (4.068 and 3.95, 3.97, 4.18 and 4.042 Å) and is shorter than in (*A*) (5.05 Å). The colours of (*B*)–(*E*) are a stronger yellow than that of (*A*). More evidence for electron density in the Te⋯Te associations comes from the larger C–Te–C angle in this compound (89.3°) and in (*B*)–(*D*) (89.7, 90.8 and 88.4°) compared with that of (*A*) (86.4°), which has weaker associations, showing that lone-pair repulsion is reduced in (*B*)–(*E*), which indicates less electron density remaining in the lone pairs.

The present structure (*E*) and structure *B* are isomorphous in that the space group of each is $P2_1$, and the cell dimensions are very similar [for (*B*): $a = 8.69$ (1), $b = 4.86$ (1), $c = 10.14$ (2) Å, $\beta = 98.7$ (1)°, $U = 423.3$ Å³]. The molecule in (*E*) has an extra methyl group on C(3), which is in an equatorial position, but apart from this (*B*) and (*E*) are isostructural. As could be expected with the extra methyl group, the volume of the unit cell for (*E*) is larger than that for (*B*). All cell dimensions for (*E*) are larger than in (*B*), except for the β angle, and the most notable change in the cell lengths is in *c*, which is greater in (*E*) by 0.9 Å. The differences between *a* and *b* for each structure are 0.11 and 0.06 Å respectively. The fact that the main change in the cell dimensions between the two structures is in the *c* direction is significant and is interpreted as showing that the packing of both (*B*) and (*E*) is controlled by the Te⋯Te associations along **b**. The effect of introducing an equatorial methyl group onto C(3) can be seen in Fig. 1 as merely serving to force each individual string of molecules further apart, since the C(3)–C(8) vector lies fairly closely along the direction of the *c* axis. The effect on the *a* and *b* dimensions is small, and the geometry of the Te⋯Te associations in (*B*) and (*E*) is consequently not very different, the Te⋯Te distances being 4.068 (7) and

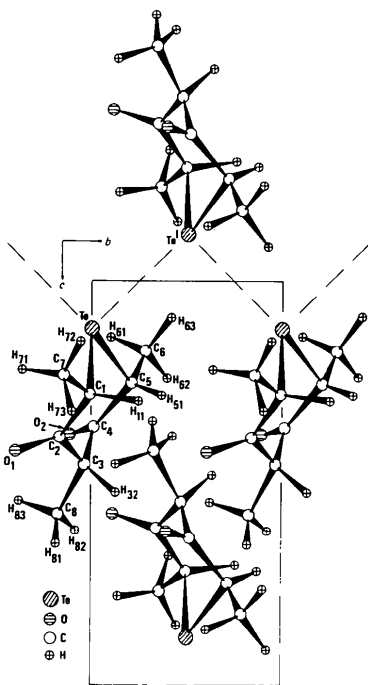


Fig. 1. Projection of the structure down a^* . The dashed line shows the zigzag arrangement of associated Te atoms.

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. C₁₀H₉N₅O, triclinic, space group *P*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*α) = 8.9 cm⁻¹ [λ(Cu *K*α₁) = 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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