

Å (Bastiansen, Fritsch & Hedberg, 1964) and for the corresponding dicarboxylic acid, 1.510 Å (Meester, Schenk & MacGillavry, 1971). However, the individual lengths within the ring show remarkable differences. Those involving the C atom which connects the amide groups are 1.527 Å and the 'back' ring bond is 1.456 Å. Similarly, in cyclopropane-1,1-dicarboxylic acid (Meester, Schenk & MacGillavry, 1971), cyclopropanecarboxamide (Long, Maddox & Trueblood, 1969) and cyclopropanecarbohydrazide (Chesnut & Marsh, 1958), the bond between the unsubstituted C atoms is the smaller one (1.462, 1.481 and 1.478 Å respectively). In all these cases, the overlapping substituent has the 'bisecting' orientation and the appropriate π orbitals are parallel.

These structural results are easily explained by the Walsh (1949) model. As shown by Hoffmann (1970), transfer of π electron density out of the Walsh orbital to a substituent will weaken the adjacent bonds for which this orbital has bonding character. The orbital has antibonding character for the bond across the ring from the point of substitution and thus that bond is strengthened by a withdrawal of electron density from the orbital. The orbitals of the substituent can only overlap with the Walsh orbital if the molecule is in the 'bisecting' orientation.

Acta Cryst. (1979), B35, 2732–2736

The Structure and Absolute Configuration of Ajugareptansin *p*-Bromobenzoate

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(Received 1 March 1979; accepted 16 July 1979)

Abstract. $C_{36}H_{47}BrO_{11}$, $M_r = 733.7$, monoclinic, $P2_1$, $a = 14.152$ (5), $b = 15.662$ (4), $c = 8.182$ (2) Å, $\beta = 93.31$ (3)°, $Z = 2$, $V = 1810$ (1) Å³, $D_m = 1.30$, $D_c = 1.35$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 1.27$ mm⁻¹. Crystals of this derivative of ajugareptansin were isolated from *Ajuga reptans*. The structure was refined to an R of 0.070 for 1591 observed reflexions. The absolute configuration was determined by the Bijvoet method. Rings *A* and *B* of the diterpene group

We are indebted to Professor Dorothy Hodgkin for many helpful comments. One of us (RU) thanks the CSIR for financial assistance.

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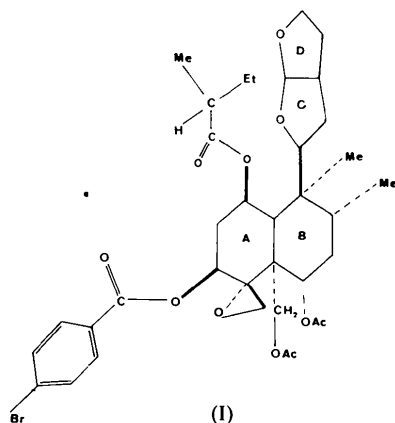
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are *trans*-fused, adopting skew-boat and chair conformations, respectively.

Introduction. Ajugareptansin is a compound isolated from *Ajuga reptans* (Camps, Coll, Cortel & Messeguer, 1979) with an antifeeding activity for insects. It is a diterpenoid with a clerodane skeleton.

A tentative structure was assigned by Camps, Coll, Cortel & Messeguer (1979) from spectral (IR, UV, mass and NMR) and chemical methods. In order to confirm this structure and to determine unambiguously its absolute configuration, we have undertaken an X-ray study of ajugareptansin *p*-bromobenzoate (I).

* Chargé de Recherches du Fonds National de la Recherche Scientifique.



A colourless prismatic crystal, $0.2 \times 0.2 \times 0.3$ mm, was used for crystal-data and intensity measurements on a Syntex four-circle diffractometer. The unit cell was measured by automatic centring of 15 independent reflexions and refining the orientation matrix and unit-cell parameters by least squares. Intensities of 2792 reflexions in the range $1 < \theta \leq 23.5^\circ$, of which 1591 were observed [$I > 2.5 \sigma(I)$], were collected with Mo $K\alpha$ radiation using the ω -scan technique with a scan interval of -0.8 to 0.8° . Lorentz-polarization corrections were carried out.

The observed systematic absences, the statistics $\langle |E|^2 - 1 \rangle$, $\langle |E| \rangle$, and the $N(z)$ distribution (Howells, Phillips & Rogers, 1950) indicated that the space group for this natural product was $P2_1$, which was confirmed by the structure determination.

The structure was solved with the *MULTAN* system of computer programs (Main, Woolfson, Lessinger, Germain & Declercq, 1978) and refined using the *SHELX* program system (Sheldrick, 1976). The final R for all observed reflexions is 0.070 ($R = \sum ||F_o| -$

Table 1. Comparison of observed and calculated $\Delta = (|F_{hkl}| - |F_{\bar{h}\bar{k}\bar{l}}|) / (|F_{hkl}| + |F_{\bar{h}\bar{k}\bar{l}}|)$ for correct absolute configuration

<i>h</i>	<i>k</i>	<i>l</i>	$1000\Delta_{\text{obs}}$	$1000\Delta_{\text{calc}}$	<i>h</i>	<i>k</i>	<i>l</i>	$1000\Delta_{\text{obs}}$	$1000\Delta_{\text{calc}}$
5	10	0	-188	-137	-3	1	1	-14	-14
2	3	0	119	109	-2	1	1	25	27
1	2	0	103	83	2	1	1	-20	-17
3	2	0	5	10	3	1	1	-58	-52
4	2	0	-29	-28	7	1	1	-25	-24
2	1	0	-57	-51	3	2	2	-28	-30
3	1	0	-121	-107	-8	1	2	-190	-105
7	1	0	-192	-142	1	1	2	75	78
-4	13	1	118	109	-4	3	3	78	72
3	11	1	140	257	-1	2	3	222	445
-12	2	1	27	53	3	2	3	54	64
-1	2	1	-50	-41	-4	1	3	74	59
0	2	1	36	38	-3	1	3	-70	-61
1	2	1	35	27	0	1	3	-60	-70
4	2	1	-83	-78	3	2	5	-44	-45
-8	1	1	-14	-7	4	2	5	71	43

$|F_c| / \sum |F_o|$)*. A difference synthesis did not reveal the peaks for the hydrogen atoms.

The absolute configuration was determined by the Bijvoet method. The structure was independently refined with the atoms in both enantiomorphic configurations; the f' and f'' values for Br, C, N and O atoms were those of Cromer & Liberman (1970).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34593 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Positional parameters ($\times 10^4$) with standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	6799 (15)	6179 (15)	4878 (26)
C(2)	6460 (14)	5815 (20)	6507 (26)
C(3)	5940 (18)	4962 (15)	6345 (33)
C(4)	5479 (17)	4830 (14)	4675 (32)
C(5)	5168 (14)	5679 (16)	3788 (26)
C(6)	4551 (15)	5493 (15)	2225 (29)
C(7)	4435 (16)	6301 (13)	1144 (24)
C(8)	5401 (18)	6651 (17)	735 (37)
C(9)	5990 (16)	6927 (17)	2278 (27)
C(10)	6094 (15)	6095 (11)	3371 (27)
O(11)	7623 (11)	5678 (13)	4440 (18)
C(12)	8469 (20)	5832 (28)	5321 (40)
O(13)	8561 (14)	6312 (16)	6375 (30)
C(14)	9241 (18)	5242 (22)	4640 (43)
C(15)	10188 (18)	5498 (24)	5425 (41)
C(16)	9046 (26)	4319 (23)	4928 (60)
C(17)	9652 (20)	3668 (22)	4033 (43)
O(18)	6544 (8)	4236 (8)	6744 (14)
C(19)	6691 (14)	4043 (13)	8342 (28)
O(20)	6377 (11)	4467 (9)	9449 (16)
C(21)	7291 (13)	3283 (14)	8559 (26)
C(22)	7561 (13)	2787 (14)	7259 (23)
C(23)	8081 (14)	2027 (12)	7533 (19)
C(24)	8342 (11)	1824 (11)	9159 (23)
C(25)	8108 (15)	2296 (14)	10473 (26)
C(26)	7562 (13)	3043 (14)	10187 (27)
Br(27)	9056 (2)	794 (1)	9514 (3)
O(28)	4919 (9)	4097 (7)	4419 (14)
C(29)	5813 (15)	4086 (12)	3606 (25)
C(30)	4532 (12)	6231 (12)	4924 (21)
O(31)	4088 (8)	5644 (8)	6009 (15)
C(32)	3203 (14)	5858 (18)	6477 (18)
O(33)	2823 (11)	6500 (12)	6094 (22)
C(34)	2856 (14)	5094 (13)	7666 (30)
O(35)	3637 (8)	5219 (8)	2698 (15)
C(36)	3304 (14)	4456 (13)	2140 (30)
O(37)	3591 (11)	4101 (9)	1026 (20)
C(38)	2470 (17)	4185 (15)	3189 (31)
C(39)	5166 (15)	7401 (13)	-546 (24)
C(40)	5562 (13)	7696 (11)	3142 (24)
C(41)	6958 (14)	7249 (11)	1680 (25)
O(42)	7543 (8)	7571 (8)	3085 (14)
C(43)	8498 (15)	7556 (14)	2680 (29)
C(44)	8598 (14)	6984 (13)	1232 (28)
C(45)	7596 (13)	6617 (13)	855 (22)
O(46)	8793 (12)	8391 (10)	2251 (26)
C(47)	8975 (19)	7594 (20)	-65 (39)
C(48)	8993 (33)	8425 (28)	677 (46)

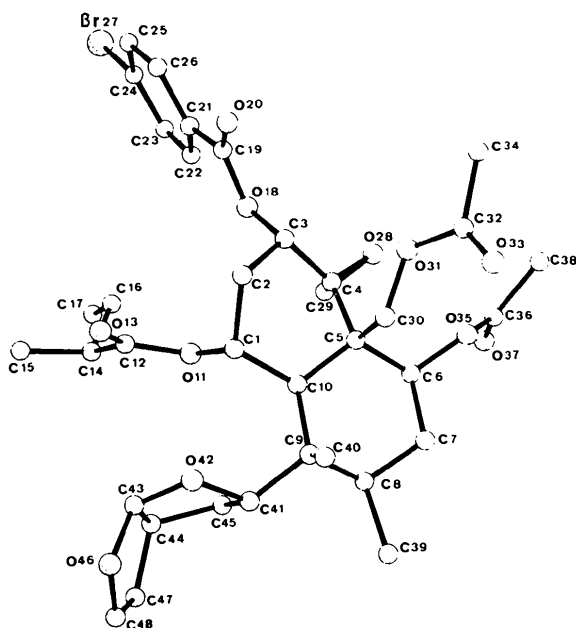


Fig. 1. Perspective view of the molecule drawn by the *PLUTO* program, and the numbering of the atoms.

Thirty two reflexions with F_c differing significantly at the end of the two refinements were remeasured with great care, hkl , $\bar{h}\bar{k}\bar{l}$, and $h\bar{k}l$ being collected. R factors were calculated for the two possible configurations. The values obtained are 0.059 for the correct absolute configuration and 0.102 for its enantiomorph. Table 1 gives the ratios $(|F_{hkl}| - |F_{\bar{h}\bar{k}\bar{l}}|) / (|F_{hkl}| + |F_{\bar{h}\bar{k}\bar{l}}|)$ for the correct configuration.

The final atomic positional parameters are listed in Table 2. The molecule in its absolute configuration is shown in Fig. 1 with atom numbering (*PLUTO*, Motherwell & Clegg, 1978).

The absolute configuration of ajugareptansin *p*-bromobenzoate is the same as that of clerodendrin A *p*-bromobenzoate chlorohydrin (II) (Kato, Munakata & Katayama, 1973). Rogers, Ūnal, Williams, Ley, Sim, Joshi & Ravindranath (1979) have shown that the configuration clerodin (III) must be reversed and its correct configuration now matches that of ajugareptansin and clerodendrin A.



Discussion. The bond lengths, bond angles and some torsion angles are shown in Figs. 2 and 3 and Table 3, respectively.

The benzene group is planar [the largest distance atom-mean plane is 0.01 (2) Å] with normal C—C distances (mean value 1.40 Å) and C—C—C bond angles (120.0°).

Rings *C* and *D* of the hexahydrofurfuran group exhibit the envelope and planar [the largest distance atom-mean plane is 0.03 (2) Å] conformations, respectively. The junction of the two rings is *cis*, with C(43)—C(44) *trans*-torsion angles of about 120° [119 (2) and -122 (2)°] as in clerodendrin A *p*-bromobenzoate chlorohydrin (Kato, Munakata & Katayama, 1973).

The two rings *A* and *B* of the diterpene group (Fig. 4) have a skew-boat and a chair form, respectively. The junction is *trans*, with C(5)—C(10) *trans*-torsion angles of 173 (2) and -172 (2)°. The conformation of these

Table 3. Selected torsion angles (°)

C(10)—C(1)—C(2)—C(3)	41 (3)	C(30)—C(5)—C(6)—C(7)	73 (2)
O(11)—C(1)—C(2)—C(3)	-75 (2)	C(30)—C(5)—C(6)—O(35)	-46 (2)
C(2)—C(1)—C(10)—C(5)	1 (3)	C(4)—C(5)—C(10)—C(1)	-53 (2)
O(11)—C(1)—C(10)—C(9)	-106 (2)	C(6)—C(5)—C(10)—C(9)	54 (2)
C(1)—C(2)—C(3)—C(4)	-26 (3)	C(30)—C(5)—C(10)—C(1)	68 (2)
C(1)—C(2)—C(3)—O(18)	98 (2)	C(30)—C(5)—C(10)—C(9)	-66 (2)
C(2)—C(3)—C(4)—C(5)	-29 (3)	C(5)—C(6)—C(7)—C(8)	56 (2)
O(18)—C(3)—C(4)—O(28)	59 (3)	C(6)—C(7)—C(8)—C(9)	-62 (2)
O(18)—C(3)—C(4)—C(29)	-9 (3)	C(7)—C(8)—C(9)—C(10)	59 (2)
C(3)—C(4)—C(5)—C(10)	71 (2)	C(7)—C(8)—C(9)—C(40)	-66 (3)
C(3)—C(4)—C(5)—C(30)	-53 (2)	C(39)—C(8)—C(9)—C(40)	53 (3)
O(28)—C(4)—C(5)—C(5)	-25 (3)	C(39)—C(8)—C(9)—C(41)	-62 (2)
O(28)—C(4)—C(5)—C(30)	92 (2)	C(8)—C(9)—C(10)—C(5)	-56 (2)
C(29)—C(4)—C(5)—C(6)	43 (2)	C(40)—C(9)—C(10)—C(1)	-65 (2)
C(29)—C(4)—C(5)—C(10)	-76 (2)	C(40)—C(9)—C(10)—C(5)	68 (2)
C(4)—C(5)—C(6)—O(35)	73 (2)	C(41)—C(9)—C(10)—C(1)	55 (2)
C(10)—C(5)—C(6)—C(7)	-52 (2)		

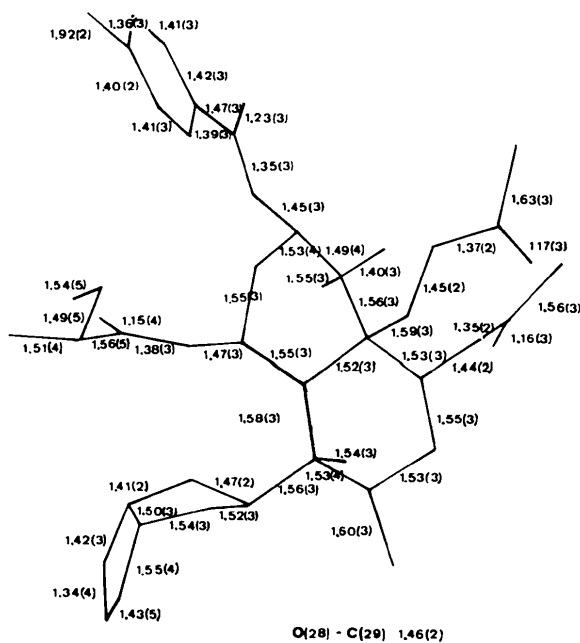


Fig. 2. Bond distances in Å.

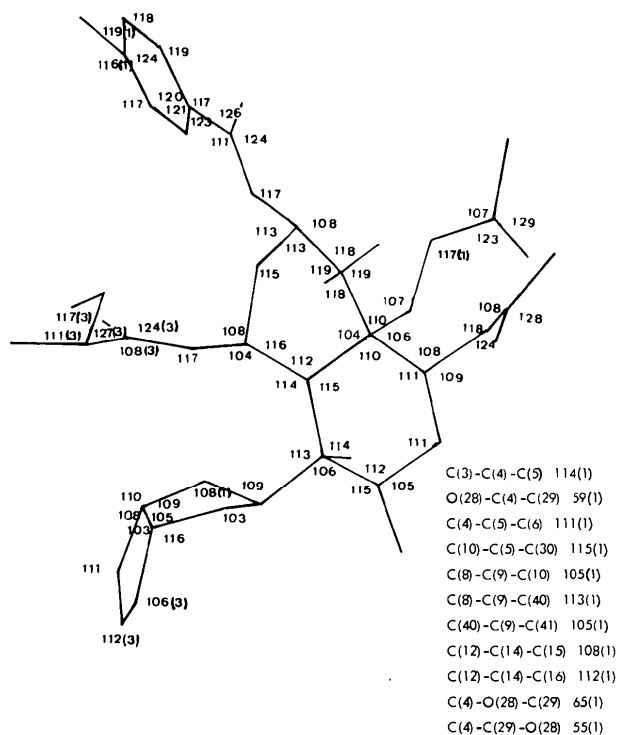


Fig. 3. Bond angles ($^{\circ}$). The standard deviations are 2° unless indicated otherwise.

two rings is chair-chair in clerodin bromolactone (Paul, Sim, Hamor & Robertson, 1962) and chair-boat in clerodendrin A *p*-bromobenzoate chlorohydrin (Kato, Munakata & Katayama, 1973), the latter being due to a double bond at C(7)-C(8).

The chair form of ring A is energetically the most favourable for a cyclohexane ring. The valence angles [range: $105.2(6)$ - $115.3(4)^{\circ}$, mean value 110.8°] and the torsion angles [$52(2)$ - $62(2)^{\circ}$, mean value: 56°] are close to those calculated by Hendrickson (1967) for the chair form of cyclohexane from a strain-energy-minimization calculation (111.6 and 54.4° respectively). The largest deviations from theoretical values are due to the C(9) atom.

The skew-boat conformation of ring A may be caused by steric interaction between the C(1) substituent group and the hexahydrofurofuran ring, which would tend to be minimized by a *gauche-gauche anti* conformation of O(11)-C(1)-C(10)-C(9)-C(41).

The other bond distances have the expected values; the large C(32)-C(34) and C(8)-C(39) distances may be due to the neglect of hydrogen atoms in the electron density model. The apparently short C(47)-C(48) and O(46)-C(48) distances are due to thermal vibration of the C(48) atom.

The short intramolecular distances (Table 4) are similar to those obtained by Paul, Sim, Hamor & Robertson (1962) in clerodin bromolactone. The

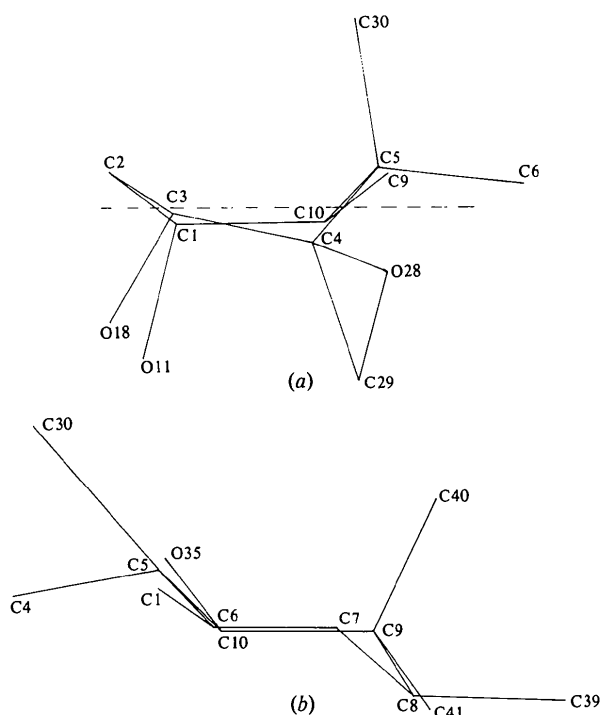


Fig. 4. Deviations of the atoms from the mean planes of rings (a) A and (b) B.

Table 4. Selected intramolecular distances (\AA) less than 3\AA

C(1)-O(42)	2.86 (3)	O(18)-C(29)	2.72 (2)
C(3)-O(31)	2.83 (3)	O(18)-O(28)	2.91 (2)
C(6)-O(28)	2.86 (3)	O(31)-O(35)	2.83 (2)

short O(18) \cdots C(29) intramolecular distance could explain some features observed in the NMR spectrum (Camps, Coll, Cortel & Messeguer, 1979). The shortest intermolecular distances are O(28)-C(40ⁱ) = $3.07(2)$, C(23)-O(33ⁱ) = $3.27(2)$, C(34)-O(37ⁱⁱ) = $3.27(3)$ and O(37)-C(39ⁱⁱⁱ) = $3.23(2) \text{\AA}$, where (i) = $1-x, y-\frac{1}{2}, 1-z$; (ii) = $x, y, z+1$; (iii) = $1-x, y-\frac{1}{2}, -z$.

We thank Drs Camps, Coll, Cortel and Messeguer for valuable discussions and for providing us with the sample of ajugareptansin *p*-bromobenzoate. One of us (CM) is grateful for the financial assistance provided by the University of Louvain and the CSIC (Consejo Superior de Investigaciones Científicas).

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Acta Cryst. (1979). **B35**, 2736–2738

Structure of Benzyl 6-Aminopurine-9-carboxylate*

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Abstract. $C_{13}H_{11}N_5O_2$, orthorhombic, $Pca2_1$, $a = 12.426$ (4), $b = 6.528$ (2), $c = 30.580$ (5) Å ($T = 295 \pm 3$ K), $V = 2480.4$ Å³, $Z = 8$ (two per asymmetric unit), $M_r = 269$, $\lambda(\text{Cu } K\alpha) = 1.54051$ Å, D_m (floatation) = 1.45, $D_x = 1.44$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 0.60$ mm⁻¹, $R = 0.058$ for 2557 reflections ($I > 2\sigma$). Molecule I is connected to molecule II by a pair of hydrogen bonds using the Watson–Crick sites N(1) and N(6). In addition, molecules I and II are linked by a single N(6)–H···N(7) hydrogen bond involving the Hoogsteen sites. The bases hydrogen bonded using Watson–Crick sites are parallel and those using Hoogsteen sites are inclined at 60° to one another.

Introduction. Reaction products of chloroformates with adenine serve as useful intermediates in the synthesis of naturally occurring ureidopurine derivatives. This structural study was undertaken to settle the assignments of the sites of acylation by chloroformates (Ohrt, Srikrishnan, Parthasarathy, Dutta & Chheda, 1978).

Crystals of the title compound were obtained by a slow evaporation from chloroform. 2866 reflections (309 had intensities $< 2\sigma$) to the limit of $2\theta = 165^\circ$ for Cu $K\alpha$ were collected using the stationary-crystal-stationary-counter procedure (Furnas & Harker,

1955) and were processed in the usual way. The difference in absorption as a function of φ (Furnas, 1957) was measured for the axial reflections and used for correcting for the anisotropy of absorption.

The crystal structure was solved by application of the multi-solution technique using *MULTAN* (Germain, Main & Woolfson, 1971). After futile attempts to solve the structure in the centrosymmetric space group *Pcam* (as suggested by the near-centrosymmetric distribution of normalized structure factors), the structure was solved readily in the noncentrosymmetric space group *Pca2₁*, and refined by least squares with a block-diagonal approximation. The H atoms were located from difference electron density maps and their parameters were refined isotropically. The refinement was carried out by minimizing $\sum w||F_o| - (1/k)|F_c||^2$ and the observations were weighted by $1/f_c$ where f_c is the scattering factor for C. Atomic scattering factors for C, N and O were taken from *International Tables for X-ray Crystallography* (1968) and for H from Stewart, Davidson & Simpson (1965). The final R factor is 0.058 for the 2557 reflections ($I > 2\sigma$). The final atomic coordinates are given in Tables 1‡ and 2.

‡ Lists of structure factors, anisotropic thermal parameters and bond distances and angles for the two molecules have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34507 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Hydrogen Bonding of Modified Adenines Involving Watson–Crick Sites.

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