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The Crystal Structure of Deoxyadenosine Monohydrate

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Deoxyadenosine crystallizes as the monohydrate in the monoclinic space group $P2_1$ with two molecules in a unit cell of dimensions: $a=16{\cdot}060\pm0{\cdot}007$, $b=7{\cdot}866\pm0{\cdot}003$, $c=4{\cdot}700\pm0{\cdot}002$ Å, $\beta=96°\ 4'\pm1'$. Angular coordinates of the plane of the adenine group and atom C(1′) of the glycosidic bond were found by integrating the Patterson function, and used in computing a superposition function from which the translational coordinates of the group were determined. The remaining atoms including the hydrogen atoms were located in three-dimensional Fourier syntheses and difference syntheses. The coordinates of the non-hydrogen atoms and the thermal parameters were refined by the full-matrix least-squares method. The final R index is 7·8 % and the standard deviations in the bond lengths and angles are about 0·01 Å and 1° respectively.

The bond lengths and angles in the base are closely similar to those in other adenine compounds. In the sugar, the only significant differences between these molecular dimensions and those in other compounds containing D-ribofuranose or 2-deoxy-D-ribofuranose occur in the exocyclic angles at C(3′). The differences are in accordance with steric hindrance between O(2′) and O(3′) in D-ribofuranose. The adenine group is planar, but the carbon atom of the glycosidic bond is displaced by 0·220 Å from this plane. The sugar ring is puckered with C(3′) displaced by 0·552 Å from the plane of the other four ring atoms so that the atom O(3′) is 1·970 Å from the plane. The dihedral angle between the sugar and base planes is 70°, and the conformation of the molecule is *anti* with the torsion angle $\varphi_{CN}=-3°$.

The packing in the crystal is determined by hydrogen bonds in which all available groups participate. The outstanding features of the system are infinite chains of N–H · · · N bonds between bases related by a screw axis, and a distorted trigonal arrangement of O–H · · · O bonds formed by the water molecule.

Introduction

The molecular structures of biological molecules are thought to be closely related to their physiological functions. Probable structures for the deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), which will help explain their essential part in protein synthesis and genetic replication, are investigated at present by the method of trial and error. The complexity of these molecules necessitates a knowledge of the molecular dimensions and of the conformation of the units comprising them. By imposing restrictions on these factors, a spatial arrangement of the molecule, compatible with the available X-ray data, is sought.

The crystal structures of many pyrimidine and purine bases and a few nucleosides and nucleotides have been published. This work has provided information on not only the molecular configuration of some of the units but also certain fairly characteristic features of the molecular packing which probably help govern the struc-

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ture of DNA itself (Langridge, Marvin, Seeds, Wilson, Hooper, Wilkins & Hamilton, 1960). These are:

(1) Pyrimidine and purine bases exhibit a great tendency to form hydrogen bonds amongst themselves and to pack in parallel planes about 3·5 Å apart.

(2) Other available groups usually participate in hydrogen bonds, and in some cases C–H · · · O hydrogen bonds are formed (Sutor, 1963).

The nucleosides and nucleotides studied so far are 5′-bromo-5′-deoxythymidine (Huber, 1957), calcium thymidylate (Trueblood, Horn & Luzzati, 1961), a cyclonucleoside (Zussman, 1953), cytidine (Furberg, 1950), cytidylic acid *b* (Alver & Furberg, 1959; Sundaralingam & Jensen, 1963), adenosine 5′-phosphate (Kraut & Jensen, 1963), 5-fluoro-2′-deoxyuridine (Harris & Macintyre, 1964) and 5-iodo-2′deoxyuridine (Camerman & Trotter, 1964). Of these, the structures of cytidylic acid *b*, 5-fluoro-2′-deoxyuridine and adenosine 5′-phosphate are the most accurately determined, having standard deviations in bond lengths and angles of the order of or less than 0·01 Å and 1° respectively. The work described here on deoxyadenosine (Fig. 1), one of the two purine nucleosides in DNA, approaches the same accuracy.

Experimental

Dr A. M. Michelson kindly provided us with two habits of crystalline deoxyadenosine monohydrate ($C_{10}H_{13}N_5O_3 . H_2O$), needles elongated along *c* and plates. Both habits were used in this investigation.

Accurate unit-cell parameters, measured with a diffractometer, are:

$$a=16{\cdot}060\pm0{\cdot}007\,,\quad b=7{\cdot}866\pm0{\cdot}003\,,$$
$$c=4{\cdot}700\pm0{\cdot}002\text{ Å}\quad \beta=96°4'\pm1'\,.$$

The errors quoted are the average deviations from the mean values. The space group is $P2_1$ (C_2^2), and the measured density of 1·510 g.cm^{-3} agrees with the calculated value 1·514 g.cm^{-3} for two molecules in the unit cell.

All possible reflexions within the range of Cu $K\alpha$ radiation were recorded on equi-inclination Weissenberg photographs (using angles up to 36°) about the *b* and *c* axes, and 10° oscillation photographs about the *a* and *c* axes. The multiple-film technique was used throughout. The intensity of each reflexion was measured visually by comparison with a standard scale, and for the Weissenberg photographs, a correlation factor for the multiple-film technique was calculated for each layer (Bullen, 1953). Where necessary, the measured intensities were corrected for the variation in spot-shape of the reflexions arising from either the non-uniform cross-section of the crystals (Broomhead, 1948), or the combination of the divergent X-ray beam on the crystal and the motion of the film (Phillips, 1954). The former correction was applied to the *hk*0 and *h*0*l* Weissenberg photographs and the latter to all upper level Weissenberg photographs. The few contracted reflexions which could not be corrected by Phillips's method were ignored since other measurements were available. The resulting intensities were converted to F^2 values (Cochran, 1948), and the layer lines were placed on the same arbitrary scale by comparison of common reflexions. Ninety-one per cent of the total number of reflexions within the Cu $K\alpha$ sphere were of measurable intensity and, for most of these, there were several independent measurements with an agreement between F^2 values of 15% or better.

Preliminary attempts at structure determination

At the commencement of this work in 1954, the stereochemistry of only one of the nucleosides and nucleotides, cytidine, was known. The size of the deoxyadenosine molecule and the absence of a heavy atom from the structure suggested a direct approach to the problem of structure determination. The method of Cochran & Douglas (1953) was used on EDSAC I to select possible sets of signs for twenty-three of the largest *h*0*l* unitary

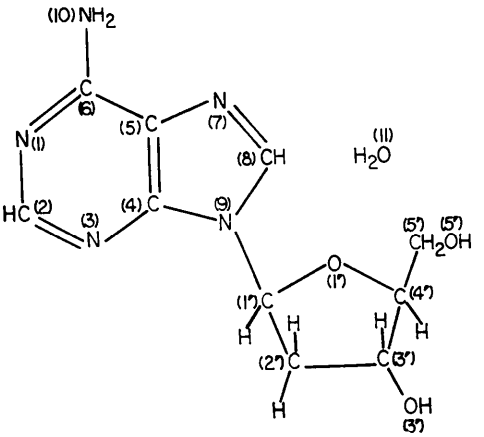

Fig. 1. The chemical constitution of deoxyadenosine monohydrate and the conventional numbering system.

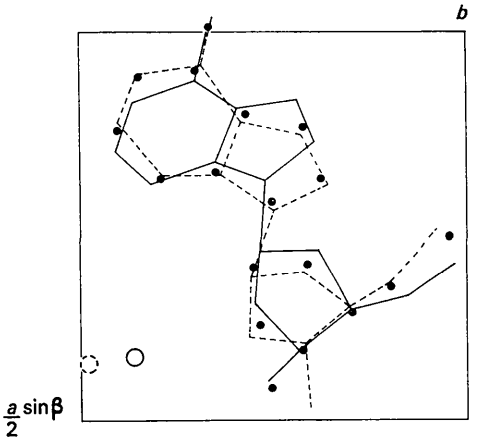

Fig. 2. Comparison of the final *x* and *y* coordinates with two trial structures. Unbroken lines: correct structure. Broken lines: structure obtained from model building (*R* value 20 %). Black dots: another trial structure which would not refine and for which the position of the water molecule could not be determined.

structure factors, U_{h0l}. Unfortunately, the correct set of signs was not recognized because of the large number of possible solutions produced by the computer, the poor resolution in the $h0l$ electron density projection, and, even allowing for an atom at the origin, the improbable sign distribution in which twenty-one of the twenty-three largest unitary structure factors were positive.

A three-dimensional Patterson series in which the terms were sharpened by the function $\exp(\sin^2\theta)$ was computed on the Hollerith Tabulator and EDSAC I. Vectors were not clearly resolved, but the probable orientation of the pyrimidine ring was found and used to propose an arrangement of molecules involving a network of hydrogen bonds identical with that described in the discussion. The resulting $hk0$ Fourier series slowly converged to an R index of 20% but could not be further improved in spite of the fact that these trial structures were apparently very close to the correct one. Two of the 'better' $hk0$ projections, one corresponding to the R index of 20%, are compared with the final atomic coordinates in Fig. 2.

Determination of the position of the purine residue

The atoms of the purine residue, which account for about 54% of the scattering by the molecule, and probably atom C(1′) of the sugar, should lie approximately in one plane. This plane might be located by the method of Tollin & Cochran (1964).

Sharpened coefficients $|F_s(\mathbf{h})|^2$ were used to compute the function

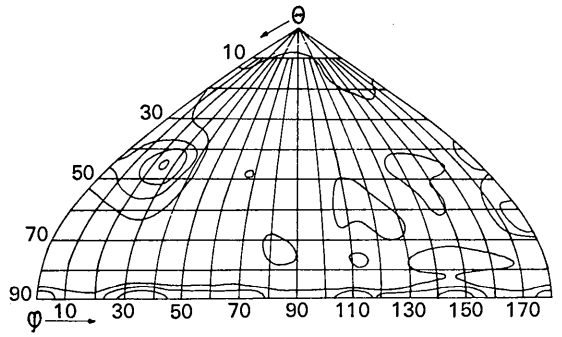

Fig. 3. Plot of $I(\theta, \varphi)$ for $R=5$ Å.

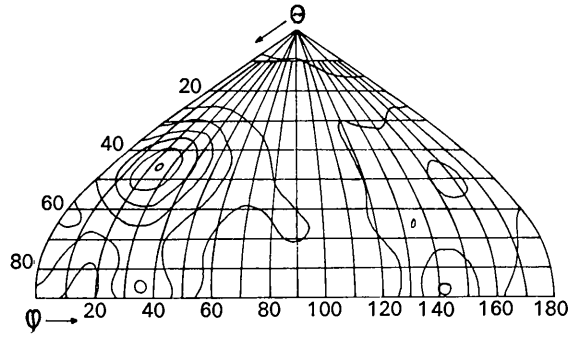

Fig. 4. Plot of $I(\theta, \varphi)$ for $R=2{\cdot}5$ Å.

$$I(\theta, \varphi)=\sum_{\mathbf{h}}|F_s(\mathbf{h})|^2 J_1(2\pi RS)/2\pi RS\,.$$

θ and φ are the spherical polar angles with respect to the axes a^*, b^* and c. R is the radius of the disc and S is the perpendicular distance of the point $\mathbf{h}$ from the normal to the disc.

The results were plotted on a Sanson–Flamsteed Sinusoidal Projection and those for $R=5$ Å, the maximum dimension of the purine residue, are shown in Fig. 3. Apart from the peaks along the line $\theta=90°$, the largest peak corresponds to $\theta=45°$, $\varphi=25°$ and probably represents the intersection of the normal to the purine plane with the sphere. The peaks along $\theta=90°$ may have resulted from the interaction of the disc with origin peaks and large intermolecular vector peaks. Since the c axis is short and the line $\theta=90°$ represents all the normals perpendicular to the c axis, these planes are likely to intersect origin peaks. A second calculation was performed with $R=2{\cdot}5$ Å and the resulting map is shown in Fig. 4. The peak at $\theta=45°$, $\varphi=25°$ again appears. However, the absence of all large peaks from the line $\theta=90°$ indicated that they were due to vectors greater than 2·5 Å in length.

The section through the Patterson function in the plane defined by $\theta=45°$, $\varphi=25°$ was calculated and a theoretical vector set for the purine residue was superimposed and rotated until the best fit was obtained. The angular coordinates of the purine residue were now known, θ and φ defining the orientation of the plane and ψ, the azimuthal angle, defining the orientation of the purine residue within the plane. The position of the purine group will then be completely defined by fixing translational coordinates of one point in it.

Since the space group is $P2_1$, only two coordinates, x and z, are required to define the position of the planar residue. Atom C(8) was arbitrarily placed at the origin and the relative fractional coordinates of the other atoms in the adenine residue were calculated from the angles θ, φ and ψ and the assumed geometry of the group. The sum function (Buerger, 1959) was calculated with these eleven positions as superposition points. This function should contain a set of maxima whose positions (x_1, y_1, z_1) are related by a 2_1 axis to the superposition points (x_0, y_0, z_0) by the equations

$$x_0+x_1=2x \qquad (1a)$$

$$y_1=\tfrac{1}{2}+y_0 \qquad (1b)$$

$$z_0+z_1=2z \qquad (1c)$$

For any given atom input at y_0 all possible pairs of peaks at the two levels y_0 and y_1 related by (1b) were considered and the values of (x, z) listed in accordance with equations (1a) and (1c). This process was repeated systematically for each of the input purine atoms. Scrutiny of the total list of (x, z) values showed that eleven pairs of peaks were consistent with equations (1a), (1b) and (1c) for $x=0{\cdot}144$, $z=0{\cdot}049$. Thus the position of the 2_1 axis was defined and the absolute coordinates of the eleven atoms could readily be calculated.

Three-dimensional structure factors calculated for the adenine group and atom C(1′) of the deoxyribose ring gave an R value of 49%, with $R(hk0)=50\%$. The coordinates of these eleven atoms were refined by $hk0$ electron density projections and a study of various models met with considerable success (Tollin, 1963). In the process of solution and refinement of the structure, the following atomic scattering factors were used: for oxygen, nitrogen and carbon, those given by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); for hydrogen, the values calculated by McWeeny (1951).

Determination of the complete structure

Structure factors calculated for the ten adenine atoms and C(1′) of the deoxyribose residue with an over-all temperature factor $B=3{\cdot}0$ Å^2 [$R(hkl)=49\%$] were used to assign phases to the terms satisfying the inequality $0{\cdot}3|F_o| \geq |F_c|$ for a three-dimensional Fourier synthesis. Inspection of the electron density map indicated the probable positions of four more atoms but, at this stage, no attempt was made to correlate these peak maxima with the chemical structure of deoxyadenosine. Accordingly, in the next structure factor calculation, the atomic scattering factors of these atoms were taken as nitrogen – a 'mean' of those for carbon and oxygen. With an over-all temperature factor $B=2{\cdot}7$ Å^2, this second structure factor calculation gave an R value of 37%. A second Fourier synthesis computed from these phase angles yielded the positions of the remaining four atoms of the asymmetric unit (excluding hydrogen atoms). Assignment of the correct atomic scattering factors to all the atoms and calculation of a third set of structure factors resulted in a decrease of R from 37% to 24%.

Refinement of the structure

The structure was refined by least-squares analysis with the Busing & Levy (1959) full-matrix IBM 704 program, and the positions of the hydrogen atoms were located in three-dimensional difference Fourier syntheses. The function minimized by least squares was $\Sigma w(F_o-F_c)^2$ and the unobserved reflexions were included with one-half the minimum observed structure amplitude. The isotropic temperature factor assigned to any hydrogen atom was in each case 0·5 unit greater than the isotropic B value of the atom to which it is covalently bonded. A single scale factor was included throughout the refinement as an adjustable parameter. The weighting scheme employed was the following:

$$\text{If } |F_o| < 5{\cdot}3,\ \sqrt{w}=1\ .$$
$$\text{If } |F_o| \geq 5{\cdot}3,\ \sqrt{w}=5{\cdot}3/|F_o|\ .$$

Sixteen low-order reflexions for which $|F_o| < |F_c|$ were given zero weight since they were considered to be affected by extinction. These reflexions are 400, 110, 210, 020, $\bar{1}01$, $\bar{2}01$, 101, 201, $\bar{3}11$, 011, 111, 311, $\bar{1}21$, $\bar{2}21$, 021, 121. Refinement of the non-hydrogen atoms was initi-

Table 1. *Positional parameters of non-hydrogen atoms and their estimated standard deviations, in fractional coordinates* $\times 10^4$

	x/a	y/b	z/c
N(1)	9042(4)	−4782(10)	−4005(15)
C(2)	8404(5)	−5202(12)	−2608(19)
N(3)	7994(4)	−4253(09)	−0884(14)
C(4)	8316(4)	−2673(10)	−0655(14)
C(5)	8982(4)	−2040(10)	−2005(16)
C(6)	9359(4)	−3212(11)	−3754(16)
N(7)	9126(4)	−0361(10)	−1308(14)
C(8)	8569(4)	−0000(11)	0437(16)
N(9)	8047(4)	−1321(09)	0837(12)
N(10)	10010(5)	−2811(10)	−5153(18)
C(1′)	7271(4)	−1349(11)	2249(14)
C(2′)	6516(4)	−1499(10)	0061(16)
C(3′)	5878(4)	−0370(11)	1250(14)
C(4′)	6434(4)	1041(09)	2659(14)
C(5′)	6572(5)	2496(12)	0676(18)
O(1′)	7202(3)	0210(08)	3692(10)
O(3′)	5494(3)	−1325(08)	3324(13)
O(5′)	7012(4)	3795(10)	2373(13)
O(11)	5798(4)	−4589(10)	5132(16)

Table 2. *Thermal parameters of non-hydrogen atoms and their estimated standard deviations*

β, as given here, is defined by $T=\exp\{-10^{-4}(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	26(2)	78(10)	465(31)	03(4)	060(7)	−04(15)
C(2)	24(2)	85(12)	515(40)	−10(5)	041(8)	−45(18)
N(3)	19(2)	68(09)	406(29)	−05(4)	043(6)	35(14)
C(4)	14(2)	76(10)	266(26)	06(4)	021(6)	−02(14)
C(5)	17(2)	71(11)	349(30)	07(4)	031(7)	18(14)
C(6)	15(2)	93(12)	356(32)	05(4)	045(7)	11(16)
N(7)	19(2)	86(10)	382(28)	−04(3)	037(6)	06(14)
C(8)	19(2)	84(11)	333(29)	01(4)	024(6)	−07(15)
N(9)	18(2)	74(09)	309(25)	02(4)	027(6)	−04(13)
N(10)	24(2)	88(11)	483(30)	−05(4)	076(6)	−03(15)
C(1′)	16(2)	94(11)	248(25)	02(4)	028(6)	03(15)
C(2′)	22(2)	81(11)	313(30)	−03(4)	020(7)	−10(15)
C(3′)	18(2)	72(10)	295(28)	−04(4)	023(6)	28(14)
C(4′)	14(2)	64(10)	313(28)	06(4)	024(6)	14(14)
C(5′)	26(2)	75(11)	395(34)	−07(5)	039(7)	19(17)
O(1′)	17(2)	92(09)	273(20)	06(3)	017(4)	−33(11)
O(3′)	19(2)	82(08)	487(27)	−04(3)	053(6)	38(14)
O(5′)	36(2)	92(09)	487(29)	−27(4)	065(7)	−34(14)
O(11)	35(2)	91(10)	672(36)	01(4)	101(8)	39(17)

Table 3. *Positional parameters with estimated standard deviations, in fractional coordinates* $\times 10^3$, *and isotropic thermal parameters for hydrogen atoms*

	x/a	*y/b*	*z/c*	*B*
H[C(2)]	824(8)	−643(20)	−297(24)	2·8 Å²
H[C(8)]	857(7)	104(18)	170(22)	2·1
H[N(10)]	1030(8)	−176(20)	−504(27)	2·7
H′[N(10)]	1024(8)	−386(20)	−591(24)	2·7
H[C(1′)]	722(6)	−237(17)	353(22)	1·9
H[C(2′)]	629(7)	−261(19)	−041(24)	2·1
H′[C(2′)]	674(7)	−110(19)	−175(24)	2·1
H[C(3′)]	552(7)	012(18)	−004(22)	2·0
H[C(4′)]	606(7)	137(17)	450(32)	1·8
H[C(5′)]	688(8)	188(18)	−114(26)	2·5
H′[C(5′)]	599(8)	306(19)	036(24)	2·5
H[O(3′)]	511(8)	−022(19)	356(23)	2·6
H[O(5′)]	729(8)	486(20)	098(25)	3·0
H[O(11)]	564(8)	−374(24)	479(29)	3·5
H′[O(11)]	601(9)	−554(21)	429(29)	3·5

ally performed with isotropic temperature factors and later with anisotropic values. Only at the end of refinement were the hydrogen positional coordinates, determined from difference syntheses, refined by least squares. A final cycle of refinement of the non-hydrogen positional and temperature parameters completed the analysis of the structure.

The final R index, from which the sixteen extinguished reflexions and the unobserved reflexions were excluded, was 7·8%. Inclusion of the unobserved reflexions resulted in $R=9{\cdot}1\%$. At the final stage the maximum positional parameter shift was 0·0045 Å, corresponding to $0{\cdot}6\sigma$, and the maximum thermal parameter shift was $0{\cdot}8\sigma$. The final positional parameters for carbon, nitrogen and oxygen are given in Table 1 and the corresponding anisotropic thermal parameters in Table 2. The positional and thermal parameters of the hydrogen atoms are listed in Table 3.

The estimated standard deviations in the positional parameters of non-hydrogen atoms range from 0·0045 Å to 0·0091 Å with an average of 0·007 Å. Interatomic distances and valence bond angles (not involving hydrogen atoms) are given in Table 4 and Fig. 5. Standard deviations of bond lengths and of bond angles not involving hydrogen atoms range from 0·008–0·001 Å with a mean value of 0·010 Å, and 0·6–1·2° with a mean of 0·8° respectively.

The location of the hydrogen atoms from difference syntheses was quite satisfactory in the sense that peaks occurred where hydrogen atoms were expected either from stereochemical considerations or from the hydrogen-bonding scheme. These peaks varied in height from 0·3–0·6 e.Å^{-3} with a mean value of 0·5 e.Å^{-3}. However, refinement of the hydrogen positional parameters by least squares results in an average estimated standard deviation of 0·13 Å in position. Thus any interatomic distance involving a hydrogen atom has a standard deviation of *ca.* 0·14 Å. Bond angles involv-

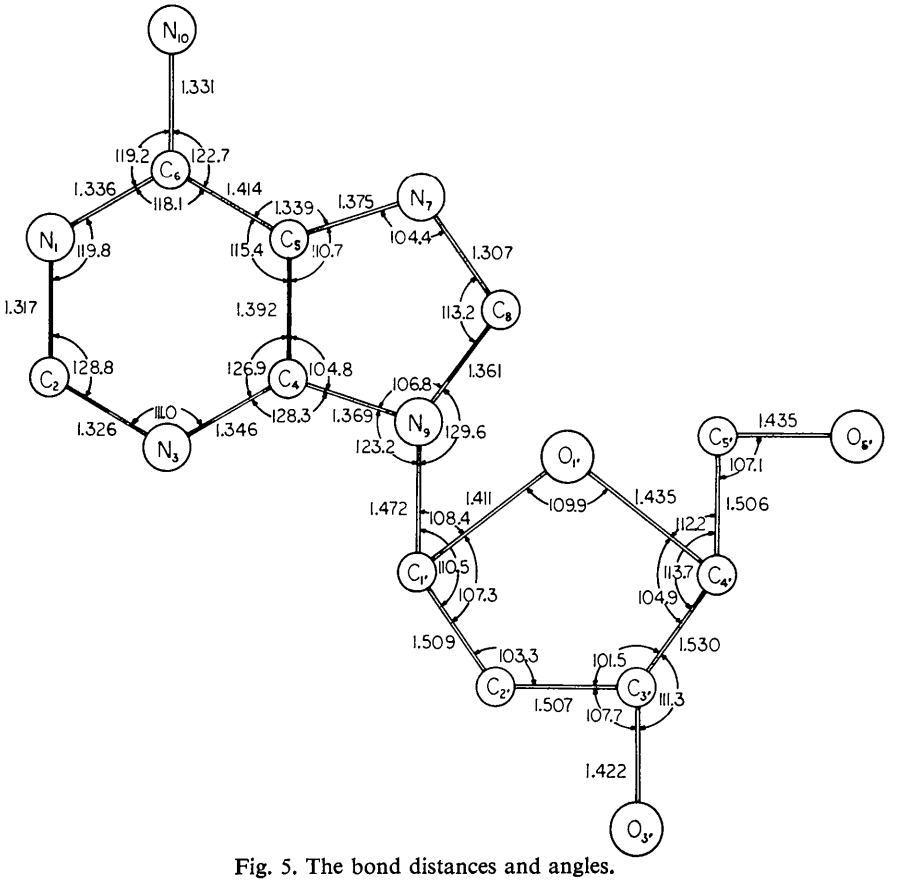

Fig. 5. The bond distances and angles.

ing one or two hydrogen atoms have standard deviations of *ca.* 11° and 25° respectively. Bond distances and angles involving hydrogen atoms are listed in Table 5.

The final three-dimensional electron density distribution is shown in Fig. 6 and the corresponding structure factors are listed in Table 6.

Discussion of the molecular and crystal structure

In comparing the molecular dimensions with other available results, data from X-ray studies of related compounds, proposed models and molecular orbital calculations are used. A discussion of the base and sugar units comprising deoxyadenosine is given, then the conformation of the molecule as a whole, the thermal vibration and mode of packing are considered.

The adenine residue

The adenine residue is strictly planar. The least-squares plane through the nine atoms of the purine group is given by

$$-0{\cdot}0716x+0{\cdot}0369y-0{\cdot}1017z+1=0\,.$$

where x, y, z refer to orthogonal axes. This plane is identical with that derived from the integration of the

Table 4. *Intramolecular bond distances and valence bond angles with the corresponding standard deviations in parentheses*

N(1)–C(2)	1·317 (0·011) Å	N(9)–C(4)	1·369 (0·010) Å
C(2)–N(3)	1·326 (0·011)	N(9)–C(1′)	1·472 (0·009)
N(3)–C(4)	1·346 (0·010)	C(1′)–C(2′)	1·509 (0·009)
C(4)–C(5)	1·392 (0·010)	C(2′)–C(3′)	1·507 (0·010)
C(5)–C(6)	1·414 (0·011)	C(3′)–C(4′)	1·530 (0·010)
C(6)–N(1)	1·336 (0·011)	C(3′)–O(3′)	1·422 (0·009)
C(6)–N(10)	1·331 (0·011)	C(4′)–C(5′)	1·506 (0·011)
C(5)–N(7)	1·375 (0·011)	C(4′)–O(1′)	1·435 (0·008)
N(7)–C(8)	1·307 (0·010)	O(1′)–C(1′)	1·411 (0·010)
C(8)–N(9)	1·361 (0·011)	C(5)′–O(5′)	1·435 (0·011)
C(6)–N(1)–C(2)	119·8 (1·0)°	C(4)–N(9)–C(1′)	123·2 (0·9)°
N(1)–C(2)–N(3)	128·8 (1·1)	C(8)–N(9)–C(1′)	129·6 (1·0)
C(2)–N(3)–C(4)	111·0 (0·9)	N(9)–C(1′)–C(2′)	110·5 (0·6)
N(3)–C(4)–C(5)	126·9 (1·0)	N(9)–C(1′)–O(1′)	108·4 (0·7)
C(4)–C(5)–C(6)	115·4 (0·9)	O(1′)–C(1′)–C(2′)	107·3 (0·7)
C(5)–C(6)–N(1)	118·1 (0·9)	C(1′)–C(2′)–C(3′)	103·3 (0·6)
N(1)–C(6)–N(10)	119·2 (1·0)	C(2′)–C(3′)–C(4′)	101·5 (0·6)
C(5)–C(6)–N(10)	122·7 (1·0)	C(3′)–C(4′)–C(5′)	113·7 (0·8)
N(3)–C(4)–N(9)	128·3 (1·0)	C(3′)–C(4′)–O(1′)	104·9 (0·6)
C(6)–C(5)–N(7)	133·9 (1·2)	O(1′)–C(4′)–C(5′)	112·2 (0·7)
C(4)–C(5)–N(7)	110·7 (0·8)	C(2′)–C(3′)–O(3′)	107·7 (0·7)
C(5)–N(7)–C(8)	104·4 (0·7)	O(3′)–C(3′)–C(4′)	111·3 (0·7)
N(7)–C(8)–N(9)	113·2 (0·9)	C(4′)–O(1′)–C(1′)	109·9 (0·7)
C(8)–N(9)–C(4)	106·8 (0·7)	C(4′)–C(5′)–O(5′)	107·1 (0·7)
N(9)–C(4)–C(5)	104·8 (0·7)		

Table 5. *Intramolecular bond distances and valence bond angles involving hydrogen atoms*

C(2)–H[C(2)]	1·0 Å	O(3′)–H[O(3′)]	1·1 Å
C(8)–H[C(8)]	1·0	C(4′)–H[C(4′)]	1·1
N(10)–H[N(10)]	0·9	C(5′)–H[C(5′)]	1·1
N(10)–H′[N(10)]	1·0	C(5′)–H′[C(5′)]	1·0
C(1′)–H[C(1′)]	1·0	O(5′)–H[O(5′)]	1·2
C(2′)–H[C(2′)]	1·0	O(11)–H[O(11)]	0·7
C(2′)–H′[C(2′)]	1·0	O(11)–H′[O(11)]	0·9
C(3′)–H[C(3′)]	0·9		
N(1)–C(2)–H[C(2)]	111°	C(3′)–C(2′)–H′[C(2′)]	116°
N(3)–C(2)–H[C(2)]	120	C(2′)–C(3′)–H[C(3′)]	115
N(7)–C(8)–H[C(8)]	126	O(3′)–C(3′)–H[C(3′)]	114
N(9)–C(8)–H[C(8)]	120	C(4′)–C(3′)–H[C(3′)]	107
C(6)–N(10)–H[N(10)]	126	C(3′)–C(4′)–H[C(4′)]	99
C(6)–N(10)–H′[N(10)]	109	O(1′)–C(4′)–H[C(4′)]	111
H[N(10)]–N(10)–H′[N(10)]	124	C(5′)–C(4′)–H[C(4′)]	115
N(9)–C(1′)–H[C(1′)]	114	C(4′)–C(5′)–H[C(5′)]	104
O(1′)–C(1′)–H[C(1′)]	113	O(5′)–C(5′)–H[C(5′)]	120
C(2′)–C(1′)–H[C(1′)]	104	H′[C(5′)]–C(5′)–H[C(5′)]	122
C(1′)–C(2′)–H[C(2′)]	119	C(4′)–C(5′)–H′[C(5′)]	103
C(3′)–C(2′)–H[C(2′)]	111	O(5′)–C(5′)–H′[C(5′)]	99
H′[C(2′)]–C(2′)–H[C(2′)]	104	C(3′)–O(3′)–H[O(3′)]	87
C(1′)–C(2′)–H′[C(2′)]	103	H[O(11)]–O(11)–H′[O(11)]	142

Table 6. *Observed and calculated structure factors*

Within each group of constant k and l, the columns contain from left to right: h, $10|F_o|$, $10F_c|$ and the phase angle in millicycles. Asterisks indicate the unobserved reflexions which were considered to have $|F_o| = 0{\cdot}5\ |F_{\min}|$. Observed values marked E were treated as extinguished reflexions and given zero weight.

H,0,0

1	95	87	000
2	180	194	500
3	78	64	500
4	280E	319	500
5	42	4	500
6	32	29	500
7	176	194	500
8	233	225	500
9	19	15	500
10	112	131	500
11	315	286	500
12	100	85	500
13	87	78	500
14	159	149	500
15	36	34	500
16	127	115	500
17	23	23	500
18	8*	5	500
19	26	21	500
20	85	81	500

H,1,0

1	253E	357	995
2	335E	434	517
3	219	224	517
4	274	286	515
5	219	223	515
6	127	125	262
7	66	56	292
8	108	90	569
9	216	204	946
10	142	134	124
11	42	30	265
12	138	137	542
13	61	62	478
14	61	51	185
15	76	73	839
16	70	71	578
17	40	44	134
18	38	42	821
19	30	33	318
20	32	43	360

H,2,0

0	320E	424	891
1	197	212	340
2	157	188	333
3	248	282	475
4	166	164	548
5	216	217	318
6	335	324	494
7	187	188	900
8	138	116	346
9	112	104	543
10	89	85	765
11	93	86	557
12	49	55	277
13	19	26	561
14	95	85	117
15	23	21	464
16	100	91	598
17	85	85	425
18	89	95	508
19	38	39	237
20	26	29	709

H,3,0

1	127	118	356
2	117	95	895
3	183	171	402
4	297	287	875
5	178	172	561
6	108	104	419
7	32	32	240
8	236	236	354
9	134	120	239
10	112	97	415
11	8*	13	361
12	180	175	312
13	57	54	285
14	98	97	112
15	45	44	557
16	100	93	539
17	40	44	583
18	40	38	776
19	53	55	900

H,4,0

0	151	151	130
1	235	259	715
2	183	174	859
3	93	88	597
4	176	162	526
5	40	31	500
6	85	72	652
7	138	130	970
8	110	108	010
9	91	82	333
10	53	50	086
11	83	74	329
12	193	200	928
13	138	143	800
14	8*	5	193
15	49	45	582
16	98	90	576
17	38	34	759
18	38	41	939
19	8*	39	997

H,5,0

1	32	31	842
2	91	81	517
3	165	152	394
4	93	93	849
5	19	18	580
6	112	105	269
7	117	117	074
8	66	66	602
9	153	165	059
10	79	76	644
11	117	113	679
12	49	53	794
13	93	90	491
14	61	52	482
15	42	39	638
16	74	69	947
17	38	37	515
18	8*	39	110

H,6,0

0	212	222	192
1	68	65	872
2	70	71	814
3	49	50	394
4	153	150	269
5	95	112	463
6	104	110	449
7	117	121	163
8	93	90	746
9	44	57	516
10	38	33	375
11	76	76	236
12	57	53	740
13	26	22	849
14	47	42	143
15	57	52	228
16	49	54	343

H,7,0

1	112	117	672
2	68	72	070
3	159	169	460
4	144	152	382
5	8*	8	772
6	38	39	594
7	95	98	858
8	91	89	976
9	83	73	968
10	49	50	441
11	32	40	061
12	38	37	742
13	78	68	311
14	68	62	217
15	8*	50	522

H,8,0

0	140	148	905
1	45	41	513
2	83	81	483
3	8*	6	101
4	144	131	317
5	96	120	690
6	108	124	871
7	66	62	048
8	8*	6	768
9	8*	11	567
10	62	62	418
11	68	66	898
12	38	38	661

H,9,0

1	26	22	658
2	26	30	977
3	62	69	544
4	45	49	052
5	32	31	588
6	8*	7	737
7	19	18	072
8	26	21	148
9	32	29	849

H,10,0

0	53	55	687
1	42	50	027
2	19	22	234
3	8*	38	277
4	8*	4	564

H,0,1

0	187	174	000
1	231E	251	500
-1	117E	235	500
2	798E	1182	500
-2	223E	240	000
3	486	529	500
-3	66	61	000
4	280	302	500
-4	299	346	500
5	189	179	500
-5	66	63	500
6	89	72	000
-6	414	505	000
7	165	160	500
-7	348	383	500
8	93	88	000
-8	255	243	500
9	95	89	000
-9	136	123	500
10	53	40	500
-10	42	34	500
11	19	19	000
-11	114	93	500
12	85	79	000
-12	85	84	500
13	189	195	500
-13	192	187	000
14	112	95	500
-14	49	45	000
15	53	48	000
-15	13	3	500
16	86	30	500
-16	89	80	500
17	19	24	500
-17	45	43	500
18	8*	7	500
-18	148	156	500
19	42	35	500
-19	19	18	500
20	8*	23	000
-20	49	47	000

H,1,1

0	327E	512	309
1	316E	406	618
-1	93	102	226
2	189	223	664
-2	185	220	999
3	469E	595	746
-3	339E	395	369
4	280	303	006
-4	112	106	887
5	316	319	098
-5	112	98	229
6	127	120	494
-6	114	103	006
7	183	191	177
-7	166	168	946
8	32	22	352
-8	49	44	883
9	38	33	045
-9	189	187	736
10	127	141	753
-10	117	114	515
-11	174	161	289
-11	98	86	966
12	95	83	498
-12	66	55	977
13	134	130	701
-13	42	38	909
14	53	59	277
-14	57	52	313
15	42	36	949
-15	149	146	165
16	42	39	876
-16	70	73	752
17	47	44	588
-17	53	64	608
18	38	35	154
-18	8*	9	383
-19	32	60	249
-19	53	50	624
-20	26	16	458

H,2,1

0	223E	310	701
1	274E	343	886
-1	216E	266	099
2	68	67	136
-2	253E	302	937
3	93	84	627
-3	231	267	748
4	199	218	121
-4	110	102	035
5	244	258	842
-5	223	227	214
6	153	142	266
-6	125	113	919
7	91	84	707
-7	178	170	199
8	161	150	927
-8	95	89	343
9	115	110	190
-9	121	113	784
10	42	34	879
-10	87	83	816
11	89	71	698
-11	98	82	429
12	62	58	675
-12	98	95	710
13	114	107	167
-13	153	149	478
14	133	117	770
-14	127	129	893
15	70	68	036
-15	123	125	905
16	42	42	847
-16	142	141	087
17	47	41	648
-17	47	49	665
18	26	25	489
-18	79	85	413
19	26	28	926
-19	8*	15	491
-20	8*	7	989

H,3,1

0	61	69	308
1	142	142	430
-1	115	117	032
2	155	175	865
-2	117	104	888
3	206	246	724
-3	333	398	368
4	125	122	270
-4	206	237	803
5	140	131	891
-5	76	66	809
6	174	182	385
-6	146	140	903
7	206	202	225
-7	98	90	084
8	87	68	020
-8	138	133	375
9	42	31	925
-9	75	75	699
10	68	53	422
-10	204	216	319
-11	49	40	564
11	117	105	813
-12	78	61	238
12	76	68	960
-13	63	53	809
13	93	88	351
-14	91	81	816
14	159	176	424
-15	74	67	709
15	76	73	901
-16	49	72	620
16	89	83	841
-17	26	21	425
17	26	24	181
-18	67	44	096
18	47	35	154
-19	8*	64	147
19	36	31	533

H,4,1

0	53	49	584
1	206	256	410
-1	144	156	066
2	32	32	868
-2	134	102	970
3	134	135	491
-3	53	53	316
4	163	169	363
-4	123	127	484
5	91	71	315
-5	68	61	377
6	153	144	137
-6	159	165	340
7	68	51	561
-7	163	161	811
8	74	65	160
-8	68	58	505
9	71	88	649
-9	61	51	569
10	132	101	560
-10	206	233	440
11	79	69	507
-11	114	113	325
12	61	56	558
-12	98	103	317
13	74	73	899
-13	98	97	139
14	102	96	447
-14	62	54	333
15	62	69	277
-15	68	52	367
16	66	52	253
-16	53	53	358
17	19	14	561
-17	42	43	459
18	36	33	178
-18	8*	8	513

H,5,1

0	127	125	483
-1	53	73	943
-1	87	75	301
2	123	125	565
-2	125	125	522
3	123	127	830
-3	172	168	216
4	26	25	244
-4	61	56	441
5	78	69	551
-5	104	103	940
6	85	78	171
-6	8*	3	185
7	114	113	217
-7	85	77	183
8	47	37	477
-8	123	133	850
9	76	74	733
-9	136	145	569
10	62	52	914
-10	91	91	403
-11	119	122	565
11	125	133	526
-12	74	73	105
12	50	32	518
13	66	65	152
-13	66	58	154
14	30	27	482
-14	74	75	552
15	53	48	749
-15	53	48	777
16	23	19	783
-16	42	43	081
17	42	52	321
-17	57	56	187

H,6,1

0	127	119	565
1	96	96	262
-1	115	101	732
2	132	110	790
-2	161	176	795
3	132	136	658
-3	79	84	002
4	85	86	423
-4	68	59	911
5	134	137	154
-5	57	53	636
6	8*	12	534
-6	227	274	220
7	78	75	831
-7	125	118	813
8	91	107	908
-8	38	34	825
9	62	57	793
-9	53	44	935
10	91	83	721
-10	26	22	459
11	88	83	196
-11	96	94	507
12	19	17	944
-12	106	102	722
13	40	41	723
-13	47	45	361
14	19	17	353
-14	95	93	836
15	8*	5	959
-15	19	14	135
16	8*	57	160
-16	32	27	594

H,7,1

0	91	83	249
-1	98	95	620
-1	112	111	350
2	57	56	786
-2	112	130	387
3	53	49	934
-3	49	49	790
4	95	98	448
-4	53	48	777
5	70	72	079
-5	121	125	808
-6	127	142	908
6	78	80	053
-7	32	29	973
7	74	74	218
-8	45	38	132
8	23	21	634
-9	30	29	420
9	32	33	068
-10	42	38	519
10	38	36	623
-11	74	68	377
11	83	75	373
-12	8*	13	702
12	38	36	127
-13	8*	8	648
13	8*	9	840
-14	8*	21	077
14	42	37	792

H,8,1

0	138	111	805
1	100	98	627
-1	78	83	455
-2	78	80	339
2	8*	7	004
3	26	26	739
-3	76	78	234
4	47	48	247
-4	87	94	391
5	57	51	973
-5	38	27	378
6	47	38	172
-6	96	130	108
7	62	56	216
-7	26	27	561
8	79	82	300
-8	26	27	148
9	42	32	430
-9	38	32	245
10	66	64	262
-10	26	23	478
11	8*	14	714
-11	49	48	511
12	8*	13	876
-12	8*	13	397

H,9,1

0	61	48	036
1	32	26	446
-1	19	18	266
2	53	48	755
-2	47	39	174
3	19	22	418
-3	79	74	596
4	19	18	539
-4	26	25	779
5	57	54	088
-5	47	39	946
6	38	30	308
-6	19	18	143
7	8*	3	728
-7	23	15	814
8	8*	51	420
-8	26	22	050
-9	8*	10	154

H,10,1

0	8*	64	667
1	8*	20	708
-1	8*	13	838
-2	8*	33	883

H,0,2

0	108	107	000
1	13	20	000
-1	96	90	000
2	142	141	000
-2	131	139	000
3	66	67	000
-3	119	126	500
4	42	39	500
-4	108	106	500
5	168	181	000
-5	369	431	000
6	191	194	000
-6	53	48	500
7	57	52	500
-7	8*	11	000
8	32	29	000
-8	38	31	500
9	57	59	000
-9	146	136	000
10	98	86	000
-10	66	58	500
11	91	87	500
-11	8*	4	000
12	8*	1	500
-12	206	225	000
13	8*	5	500
-13	93	81	000
14	53	50	500
-14	153	161	000
-15	61	60	000
-15	66	71	000
16	8*	13	000
-16	57	50	000
17	49	51	000
-17	42	37	500
18	8*	2	500
-18	53	47	500
-19	19	18	000

H,1,2

0	183	181	662
1	85	83	607
-1	131	145	960
2	183	192	727
-2	68	65	392
3	89	88	981
-3	202	230	745
4	85	86	935
-4	53	49	297
5	392	426	205
-5	206	203	349
6	208	201	367
-6	140	141	256
7	144	136	606
-7	134	118	188
8	62	54	674
-8	79	72	192
9	62	53	574
-9	153	160	448
10	49	36	017
-10	13	5	060
11	106	100	713
-11	163	160	671
12	70	65	273
-12	138	141	706
13	38	36	757
-13	93	94	977
14	42	37	970
-14	66	69	123
15	45	48	175
-15	104	105	111
16	66	63	957
-16	66	70	105
17	19	18	467
-17	68	70	044
18	49	59	635
-18	42	43	720
-19	26	25	385

H,2,2

0	212	175	280
1	144	128	630
-1	127	112	264
2	95	96	267
-2	45	37	648
3	174	162	238
-3	331	365	627
4	250	254	366
-4	104	98	048
5	136	132	489
-5	182	189	755
6	265	261	607
-6	183	185	490
7	153	142	264
-7	261	261	199
8	127	111	791
-8	112	98	499
9	42	31	074
-9	85	70	784
10	121	116	099
-10	104	105	300
11	74	70	612
-11	119	118	345
12	83	82	580
-12	49	45	388
13	26	31	436
-13	153	165	412
14	53	52	151
-14	125	127	659
15	30	24	665
-15	26	28	166
16	38	35	488
-16	57	55	994
17	61	56	635
-17	42	41	495
18	49	51	379
-18	38	39	381
-19	32	29	024

H,3,2

0	89	92	905
1	176	190	582
-1	178	156	912
2	19	19	268
-2	246	289	327
3	38	33	773
-3	108	104	010
4	100	94	501
-4	118	111	118
5	117	117	125
-5	79	73	369
6	74	67	280
-6	100	87	857
7	42	33	057
-7	76	68	029
8	114	105	906
-8	23	7	798
9	57	40	724
-9	176	179	347
10	97	87	655
-10	176	175	815
11	62	57	749
-11	153	154	776
12	23	14	043
-12	112	121	948
13	55	41	354
-13	93	92	435
14	32	31	815
-14	57	56	349
15	38	42	436
-15	42	41	052
16	19	16	365
-16	125	136	373
17	45	52	203
-17	85	86	980
-18	42	41	859

H,4,2

0	180	183	009
1	159	144	633
-1	8*	9	682
2	85	79	488
-2	98	93	994
3	231	230	991
-3	91	78	656
4	42	36	573
-4	138	103	898
5	52	61	562
-5	138	96	967
6	38	25	773
-6	38	31	002
7	96	94	964
-7	134	134	009
8	104	89	675
-8	110	99	931
9	45	42	051
-9	57	57	595
10	68	56	955
-10	115	114	511
11	61	59	622
-11	126	125	992
12	36	27	452
-12	26	24	992
13	32	31	157
-13	91	92	791
14	70	67	141
-14	79	75	850
15	8*	9	306
-15	19	10	915
16	8*	5	867
-16	19	13	544
17	8*	15	852
-17	45	45	947
-18	32	29	771

H,5,2

0	108	102	677
1	144	155	622
-1	123	123	612
2	61	52	178
-2	110	105	067

Table 6 (*cont.*)

3	19	11	444
-3	68	51	787
4	115	109	536
-4	110	112	503
5	125	120	398
-5	70	51	561
6	52	5	346
-6	146	164	393
7	121	121	544
-7	134	146	121
8	45	44	466
-8	125	133	442
9	56	53	792
-9	125	132	265
10	53	51	301
-10	108	103	714
11	19	14	535
-11	125	128	575
12	23	13	322
-12	32	26	431
13	62	52	265
-13	36	23	944
14	26	26	475
-14	36	28	788
15	38	34	717
-15	49	47	554
16	8*	21	566
-16	68	64	295
-17	26	24	270

H,0,2

0	78	92	272
1	52	51	214
-1	76	68	403
2	149	155	195
-2	134	155	222
3	62	59	765
-3	61	67	512
4	83	87	753
-4	151	171	348
5	74	67	562
-5	117	114	282
6	79	8	161
-6	62	52	478
7	74	59	725
-7	53	45	467
8	53	52	824
-8	115	114	235
9	13	11	263
-9	121	110	183
10	32	33	554
-10	40	35	269
11	38	43	353
-11	32	23	454
12	66	72	335
-12	85	76	258
13	8*	9	523
-13	57	57	741
14	26	22	132
-14	38	32	335
-15	32	25	743

H,7,2

0	120	96	932
1	61	62	589
-1	93	95	315
2	45	41	789
-2	45	41	298
3	8*	3	942
-3	62	58	563
4	19	18	769
-4	53	54	544
5	66	7	293
-5	89	86	789
6	13	17	781
-6	38	39	413
7	53	54	904
-7	26	23	559
8	53	45	699
-8	32	23	355
9	32	34	462
-9	32	32	222
10	32	30	503
-10	8*	6	785
11	26	27	842
-11	85	72	589
12	8*	13	789
-12	23	9	114
-13	26	2	905

H,8,2

0	13	13	554
1	58	77	325
-1	45	44	775
2	62	73	130
-2	53	57	654

3	53	49	451
-3	42	58	522
4	49	41	525
-4	62	55	614
5	42	39	543
-5	57	53	003
6	42	44	926
-6	57	63	751
7	45	40	388
-7	26	30	485
8	53	50	695
8	91	81	126
9	38	38	759
-9	57	47	935
10	8*	44	767
-10	42	33	613
-11	19	44	483

H,9,2

0	26	29	985
1	32	32	359
-1	45	45	146
2	66	66	510
-2	23	23	318
3	38	32	554
-3	26	20	810
4	26	19	099
-4	19	20	785
5	26	26	952
-5	19	20	261
6	8*	14	327
-6	38	36	576
-7	8*	11	095

H,0,3

0	36	32	000
1	100	100	500
-1	26	24	500
2	96	95	500
-2	57	54	500
3	38	31	500
-3	32	22	500
4	102	99	500
-4	123	107	000
5	108	97	500
-5	8*	7	500
6	57	61	000
-6	95	103	000
7	32	31	500
-7	76	72	500
8	23	21	000
-8	102	91	500
9	13	4	500
-9	131	132	500
10	68	63	500
-10	250	289	500
11	23	25	000
-11	66	63	000
12	61	59	500
-12	87	87	500
13	13	7	000
-13	8*	9	500
14	8*	6	500
-14	66	69	000
15	13	16	000
-15	13	12	000
16	13	10	000
-16	42	39	500
-17	13	15	000
-18	45	43	000

H,1,3

0	155	144	283
1	49	47	686
-1	87	77	273
2	57	59	156
-2	180	180	741
3	13	11	883
-3	102	94	844
4	57	54	177
-4	49	54	752
5	8*	8	348
-5	23	19	136
6	26	23	339
-6	115	117	782
7	61	64	557
-7	140	148	109
8	83	80	798
-8	32	40	794
9	57	54	822
-9	119	119	091
10	96	88	140
-10	174	181	190
11	32	30	879
-11	74	64	633
12	53	49	700

-12	76	84	536
13	42	35	174
-13	132	134	701
14	8*	15	333
-14	26	27	932
15	8*	20	265
-15	76	82	460
16	8*	9	976
-16	49	49	022
-17	19	20	969
-18	26	20	694

H,2,3

0	8*	5	738
1	104	105	044
-1	168	157	183
2	119	112	720
-2	53	44	447
3	66	61	637
-3	127	125	159
4	95	91	266
-4	202	206	895
5	57	59	528
-5	159	155	597
6	168	161	749
-6	169	169	108
7	106	99	929
-7	26	20	024
8	199	216	869
-8	114	127	610
9	49	45	867
-9	119	130	692
10	38	36	335
-10	115	108	112
11	d*	6	423
-11	123	126	964
12	79	79	529
-12	70	58	146
13	d*	7	549
-13	74	76	982
14	26	26	175
-14	62	54	767
15	8*	11	981
-15	13	11	887
16	8*	11	490
-16	38	28	863
-17	32	32	271
-18	26	26	946

H,3,3

0	32	34	028
1	87	87	981
-1	110	107	528
2	61	56	671
-2	76	60	316
3	96	94	174
-3	62	57	976
4	57	52	524
-4	61	53	399
5	61	60	890
-5	8*	9	334
6	100	90	991
-6	127	106	877
7	92	87	318
-7	42	37	176
8	32	26	947
-8	201	221	333
9	32	32	469
-9	86	77	002
10	62	60	472
-10	57	55	567
11	38	29	621
-11	26	25	263
12	8*	13	040
-12	26	28	817
13	8*	6	698
-13	74	74	718
14	42	40	291
-14	42	40	909
15	19	15	200
-15	93	93	429
-16	66	55	822
-17	49	49	002

H,4,3

0	45	44	377
1	114	127	959
-1	61	57	475
2	176	195	477
-2	57	50	721
3	43	32	379
-3	57	55	168
4	114	115	107
-4	89	86	606
5	66	61	402
-5	61	52	551

6	42	37	504
-6	114	116	090
7	44	36	084
-7	36	28	070
8	57	60	024
-8	79	71	380
9	19	21	467
-9	163	173	480
10	23	15	760
-10	44	45	258
11	32	28	445
-11	76	67	285
12	19	15	480
-12	49	42	355
13	45	41	469
-13	70	71	041
14	38	35	331
-14	32	32	965
15	8*	15	980
-15	87	87	408
-16	26	23	582

H,5,3

0	104	113	441
1	38	37	081
-1	98	94	498
2	42	36	204
-2	117	129	001
3	119	133	111
-3	68	68	629
4	49	48	865
-4	79	82	952
5	38	41	837
-5	85	89	663
6	62	66	541
-6	79	78	640
7	38	34	018
-7	38	39	974
8	26	19	976
-8	132	141	160
9	49	45	663
-9	26	24	069
10	38	36	727
-10	70	65	610
11	61	54	455
-11	36	32	296
12	23	21	173
-12	42	35	469
13	8*	5	347
-13	74	65	835
-14	36	29	845
-15	13	11	365

H,6,3

0	70	74	134
1	83	78	913
-1	61	59	375
2	23	22	614
-2	30	28	389
3	49	46	671
-3	45	46	974
4	74	72	590
-4	85	86	932
5	78	77	620
-5	66	61	847
6	19	21	026
-6	100	104	756
7	43	38	991
-7	61	59	688
8	76	71	825
-8	52	50	411
9	23	22	237
-9	26	29	741
10	30	27	524
-10	32	27	698
11	26	25	203
-11	32	38	298
12	8*	17	294
-12	40	36	708
-13	61	52	111

H,7,3

0	57	48	504
1	30	28	768
-1	70	69	424
2	13	10	363
-2	8*	9	020
3	13	9	930
-3	78	66	333
4	26	24	511
-4	49	42	003
5	62	57	987
-5	38	31	789
6	32	32	369
-6	76	64	959
7	13	8	702

-7	45	44	180
8	45	39	141
-8	23	17	564
9	53	27	561
-9	79	69	380
10	8*	9	446
-10	38	27	431
-11	42	47	533

H,8,3

0	53	53	017
1	49	51	235
-1	38	33	933
2	32	28	731
-2	19	22	398
3	23	22	556
-3	42	42	341
4	56	56	920
-4	26	27	224
5	8*	12	999
-5	8*	13	944
6	8*	4	908
-6	45	43	593
-7	32	36	577
-8	8*	3	172

H,0,4

0	13	8	500
1	13	4	500
-1	76	74	500
2	23	26	500
-2	19	12	500
3	136	126	500
-3	26	22	500
4	8*	2	500
-4	42	38	500
5	9*	9	500
-5	42	45	500
6	79	78	500
-6	165	159	500
7	8*	12	500
-7	114	103	500
8	8*	5	500
-8	183	186	500
9	26	31	500
-9	8*	15	500
10	26	26	500
-10	110	107	500
11	13	4	500
-11	8*	3	500
12	26	23	500
-12	26	29	500
13	13	7	500
-13	13	9	500
14	8*	4	500
-14	44	49	500
-15	31	31	500
-16	13	12	500

H,1,4

0	78	77	271
1	45	45	194
-1	40	38	539
2	78	72	887
-2	8*	1	109
3	42	36	733
-3	79	84	518
4	38	38	999
-4	26	27	242
5	66	67	864
-5	62	62	584
6	26	24	557
-6	129	134	348
7	19	17	948
-7	32	42	515
8	43	41	295
-8	125	132	728
9	42	43	762
-9	132	133	144
10	19	21	935
-10	57	58	950
11	13	10	261
-11	19	18	399
12	40	46	984
-12	19	25	970
13	13	18	329
-13	32	42	942
14	8*	17	278
-14	45	54	510
-15	8*	9	716
-16	30	40	204

H,2,4

0	74	72	568
1	49	48	725

-1	32	29	512
2	42	43	083
-2	119	112	307
3	57	58	655
-3	62	55	546
4	62	56	400
-4	117	106	735
5	61	56	207
-5	98	96	178
6	38	31	910
-6	87	77	044
7	32	36	712
-7	38	40	255
8	42	47	134
-8	110	108	560
9	48	52	247
-9	49	52	401
10	70	73	501
-10	89	82	490
11	42	50	548
-11	68	72	441
12	19	23	511
-12	57	57	211
13	19	23	024
-13	8*	7	933
-14	32	36	543
-15	66	62	664

H,3,4

0	68	59	882
1	76	68	182
-1	87	79	632
2	62	56	795
-2	23	13	246
3	49	44	140
-3	49	44	588
4	62	54	334
-4	38	39	700
5	8*	7	346
-5	66	61	903
6	53	50	019
-6	32	30	995
7	23	15	062
-7	62	62	240
8	68	70	390
-8	26	27	978
9	49	39	649
-9	70	68	857
10	53	51	723
-10	23	22	485
11	53	57	775
-11	32	29	368
12	23	29	091
-12	45	45	916
-13	32	24	054
-14	98	96	326
-15	45	49	716

H,4,4

0	70	69	412
1	53	48	985
-1	61	51	830
2	66	63	104
-2	70	70	086
3	93	89	410
-3	91	84	523
4	70	70	918
-4	97	91	630
5	57	57	961
-5	100	100	990
6	55	52	755
-6	89	84	926
7	45	47	825
-7	78	74	990
8	26	17	645
-8	32	26	682
9	36	29	987
-9	36	31	949
10	26	21	825
-10	61	53	588
11	30	24	565
-11	53	57	551
-12	26	24	107
-13	70	68	874
-14	13	11	877

H,5,4

0	49	52	476
1	53	57	187
-1	19	16	358
2	42	40	869
-2	49	46	227
3	53	53	889
-3	19	11	250
4	26	25	753
-4	8*	7	703

5	53	56	577
-5	13	13	643
6	32	32	446
-6	78	77	511
-7	19	17	312
7	78	75	155
8	42	41	187
-8	70	68	522
9	8*	6	572
-9	45	41	657
10	8*	28	804
-10	26	25	011
-11	8*	18	460
-12	8*	4	535

H,6,4

0	26	21	377
1	32	30	822
-1	36	36	545
2	30	29	022
-2	76	78	431
3	42	42	337
-3	49	53	359
4	44	42	582
-4	49	46	155
-5	23	22	156
6	32	32	938
-6	19	23	921
7	49	51	910
-7	26	39	187
8	26	28	277
-8	8*	9	986
-9	23	21	246
10	38	29	092
-10	32	30	341

H,7,4

0	32	34	953
1	8*	7	745
-1	38	39	825
2	38	48	063
-2	45	54	509
3	49	48	914
-3	32	36	996
4	32	34	596
-4	42	40	440
-5	8*	21	154
-5	8*	18	499
-6	8*	13	318
-7	8*	13	797

H,0,5

0	13	12	500
1	38	33	500
-1	13	5	500
2	13	12	500
-2	13	17	500
3	42	43	000
-3	32	35	500
4	61	65	000
-4	98	89	500
5	102	97	500
-5	100	94	500
6	19	13	500
-6	68	66	500
7	8*	1	000
-7	8*	4	000
8	13	11	500
-8	96	89	500
9	8*	3	000
-9	42	46	500
10	8*	9	500
-10	13	15	500
-11	8*	12	000
-12	26	24	500

H,1,5

0	23	27	378
1	26	27	119
-1	66	65	136
2	23	21	994
-2	23	23	738
3	23	16	394
-3	85	82	805
4	40	45	642
-4	112	116	923
5	19	13	276
-5	13	19	426
6	36	42	326
-6	38	41	419
7	26	32	846
-7	36	41	602
8	19	25	975
-8	57	60	282
9	19	27	574

-9	32	35	163
-10	19	29	861
-11	23	25	455
-12	42	46	183

H,2,5

0	26	20	711
1	19	15	707
-1	53	48	171
2	26	33	047
-2	16	12	402
3	19	24	074
-3	89	85	754
4	8*	7	922
-4	49	47	066
5	26	30	470
-5	26	22	110
6	23	24	986
-6	56	64	890
7	22	22	020
-7	26	27	918
8	32	35	744
-8	38	42	986
9	8*	11	195
-9	57	53	715
-10	8*	14	758
-11	38	40	096

H,3,5

0	8*	9	061
1	51	53	096
-1	30	31	243
2	38	36	342
-2	49	49	377
3	8*	6	470
-3	52	58	653
4	8*	14	457
-4	61	65	792
5	19	21	752
-5	40	37	488
6	19	12	010
-6	19	18	220
7	26	28	782
-7	61	51	275
8	8*	22	665
-8	23	23	157
-9	26	23	086
-10	42	45	591

H,4,5

0	23	20	314
1	36	33	457
-1	57	53	034
2	8*	11	932
-2	32	30	359
3	8*	11	235
-3	74	72	461
4	32	35	743
-4	13	13	195
5	36	39	738
-5	13	10	423
6	8*	11	547
-6	23	22	620
-7	32	26	406
-8	51	54	085
-9	19	13	614

H,5,5

0	19	17	578
1	32	31	971
-1	30	35	351
2	8*	9	329
-2	23	26	980
-3	19	27	801
4	38	41	737
-4	8*	5	905
-5	23	27	827
6	49	50	624
-6	19	18	473

H,0,6

0	8*	32	500
1	8*	7	000
-1	8*	34	500
-2	8*	54	000
3	8*	64	000
-4	8*	8	500

H,1,6

0	8*	31	370
-1	8*	41	332
-2	8*	48	515
-3	8*	28	039

Patterson function. Deviations of the nine atoms from the plane are not significant. The maximum value is 0·019 Å for N(9) and the root mean square deviation is 0·010 Å. Of the substituent atoms, N(10) with a deviation of 0·016 Å is coplanar but C(1′) of the glycosidic link is displaced by 0·220 Å corresponding to an angle of about 9° between this bond and the adenine group. Large displacements of C(1′) from the plane of the base have also been found in adenosine-5′-phosphate and in the nucleotide-like residue in vitamin B_{12} (Hodgkin, Lindsey, Sparks, Trueblood & White, 1962) where the corresponding values are 0·211 and 0·42 Å. In the pyrimidine nucleosides and nucleotides studied, C(1′) is coplanar with the base in cytidine and cytidylic acid *b* (Alver & Furberg, 1959) and 5-iodo-2′-deoxyuridine, and it is displaced by only 0·05 Å in calcium thymidylate. These studies are of limited accuracy but in the recent refinement of cytidylic acid *b* (Sundaralingam & Jensen, 1963) it is indeed observed that C(1′) is coplanar with the base. However, in the analysis of 5-fluoro-2′-deoxyuridine it is found that C(1′) is significantly displaced from the pyrimidine plane by 0·150 Å.

A quantitative interpretation of the bond lengths in terms of resonance forms is not possible. The large contribution of charged forms necessary to explain the 'short' C(6)–N(10) bond is not compatible with the contribution of those required to account for the bond lengths in the pyrimidine ring. In the pyrimidine and purine systems this exocyclic C–N bond has always been observed to be 'short', as is shown by a comparison of the values cited in Table 7 with 1·43 Å for a C–N bond involving a trigonally hybridized carbon atom. However, the glycosidic bond N(9)–C(1′) of length 1·468 Å agrees well with 1·47 Å for a C–N single bond, and with 1·492 Å in adenosine-5′-phosphate, 1·466 Å in calcium thymidylate and 1·476 Å in the refined structure of cytidylic acid *b*. The analogous bonds in 9-methyladenine (Stewart & Jensen, 1964) and 1-methylthymine–9-methyladenine (Hoogsteen, 1963) also compare well with values of 1·468 and 1·453 Å respectively.

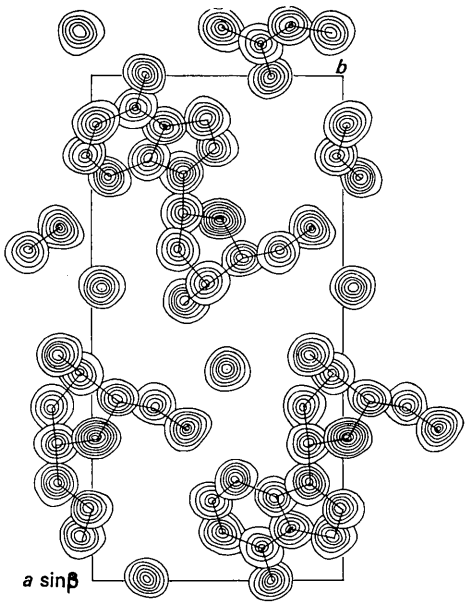

Fig. 6. Composite three-dimensional electron density distribution viewed down the *c* axis.

The most accurate structure analyses of adenine derivatives available for comparison are adenosine-5′-phosphate, 9-methyladenine and 1-methylthymine–9-methyladenine. Table 8 shows the bond lengths and angles in these three compounds and deoxyadenosine. Within the limits of precision quoted for these studies, various individual differences are probably not significant apart from those for the C(6)–N(1) and N(1)–C(2) bonds. The lengthening of these bonds in adenosine-5′-phosphate is in accordance with N(1) being protonated in this compound.

Pauling & Corey (1956) and Spencer (1959) have used data from known crystal structures to predict molecular dimensions for the units of the nucleic acids and related compounds. More information was available for the latter study and good agreement for pyrimidine rings has been obtained, but the manner of fusion of the five- and six-membered rings and mutual compensation in angular strain complicates the purine system. The bond lengths in the pyrimidine ring of deoxyadenosine agree well with those suggested by Spencer but discrepancies in some of the experimental and predicted bond angles are quite large.

Pullman & Pullman (1958) and Fernandez-Alonso & Sebastian (1960) using molecular orbital calculations have derived bond lengths for the adenine molecule. These values agree with those found here with two exceptions. The former workers report 1·38 Å for the C(6)–N(10) bond which, compared with the values in Table 7, is longer than expected. Fernandez-Alonso & Sebastian quote 1·33 Å for the C(8)–N(9) bond which

Table 7. *Length of the* C–NH_2 *bond in some related compounds*

Deoxyadenosine	1·331 ± 0·011 Å	
Adenosine-5′-phosphate	1·312 ± 0·013	(Kraut & Jensen, 1963)
Adenine hydrochloride	1·30 ± 0·01	(Cochran, 1951)
9-Methyladenine	1·348 ± 0·009	(Stewart & Jensen, 1964)
1-Methylthymine–9-methyladenine	1·335 ± 0·005	(Hoogsteen, 1963)
Cytosine monohydrate	1·332 ± 0·012	(Jeffrey & Kinoshita, 1963)
Cytosine-5-acetic acid	1·323 ± 0·006	(Marsh, Bierstedt & Eichhorn, 1962)
Cytidylic acid *b*	1·323 ± 0·006	(Sundaralingam & Jensen, 1963)
Guanine hydrochloride	1·32 ± 0·01	(Broomhead, 1951)
Thiamine hydrochloride	1·316 ± 0·007	(Kraut & Reed, 1962)

is significantly shorter than the values listed in Table 8 apart from that for 9-methyladenine.

The deoxyribose ring

Strain in the furanose ring caused by a planar arrangement of the five atoms and close intramolecular contacts between exocyclic substituents can be relieved by puckering the ring in such a way that C(2′) or C(3′) is displaced from the plane of the other four atoms by about 0·5 Å (Spencer, 1959). In systems so far studied where the displaced atom carries an oxygen atom, this oxygen atom is brought into or close to this plane. However, in deoxyadenosine C(3′) is displaced by 0·552 Å and O(3′) by 1·970 Å from the least-squares plane through atoms C(1′), C(2′), C(4′) and O(1′). In the 2-deoxyribofuranose system there is no reason to expect preferential puckering of the oxygen atom attached to C(3′) toward the plane rather than away from it and one can only assume that the buckling occurs in such a manner as best to fit the special packing considerations such as intermolecular hydrogen bonding.

The equation of the 'best' plane in deoxyadenosine is

$$-0{\cdot}1063x-0{\cdot}0906y+0{\cdot}1289z+1=0\,,$$

where x, y, z are orthogonal coordinates. Deviations of the atoms C(1′), C(2′), C(4′) and O(1′) from this plane are 0·013, −0·007, 0·008 and −0·013 Å respectively. This plane differs by only 5° from that corresponding to one of the smaller peaks in the map shown in Fig. 3. When planes are calculated for the five ring atoms or for the other four groups of four atoms, the root mean square deviation is between 0·1 and 0·2 Å.

The average length of the C–C bonds is 1·513 Å. All the observed values in deoxyadenosine are smaller, and those for C(1′)–C(2′) and C(2′)–C(3′) are significantly smaller, than a C–C bond of 1·54 Å. They support the value of 1·53 Å suggested by Bartell (1959) for the C–C bond in saturated hydrocarbons. The average length of the four C–O bonds, 1·426 Å, is in excellent agreement with the accepted single bond length of 1·43 Å.

Apart from a few exocyclic angles, the bond angles are closely similar to those in 5-fluoro-2′-deoxyuridine, calcium thymidylate, adenosine-5′-phosphate and cytidylic acid *b* (Table 9), and to those predicted by Spencer. The close similarity between bond distances and angles in calcium thymidylate and adenosine-5′-phosphate led Kraut & Jensen (1963) to conclude that there are no differences in the structures of D-ribofuranose

Table 8. *Comparison of bond distances and angles in the adenine group of deoxyadenosine* (WST), *adenosine-5′-phosphate* (KJ), *1-methylthymine–9-methyladenine* (H) *and 9-methyladenine* (SJ)*

	WST	KJ	H	SJ
N(1)–C(2)	1·317 Å	1·368 Å	1·361 Å	1·348 Å
C(2)–N(3)	1·326	1·312	1·304	1·322
N(3)–C(4)	1·346	1·341	1·347	1·338
C(4)–C(5)	1·392	1·403	1·373	1·365
C(5)–C(6)	1·414	1·448	1·406	1·395
C(6)–N(1)	1·336	1·362	1·355	1·348
C(6)–N(10)	1·331	1·312	1·335	1·348
C(5)–N(7)	1·375	1·364	1·381	1·379
N(7)–C(8)	1·307	1·328	1·323	1·311
C(8)–N(9)	1·361	1·398	1·363	1·354
N(9)–C(4)	1·369	1·377	1·389	1·359
†N(9)–C(1′)	1·472	1·492	1·453	1·468
C(6)–N(1)–C(2)	119·8°	122·8°	116·8°	119·8°
N(1)–C(2)–N(3)	128·8	125·7	130·9	126·5
C(2)–N(3)–C(4)	111·0	112·3	109·9	112·4
N(3)–C(4)–C(5)	126·9	128·5	127·4	126·6
C(4)–C(5)–C(6)	115·4	115·6	116·9	117·2
C(5)–C(6)–N(1)	118·1	114·7	118·0	117·4
N(10)–C(6)–N(1)	119·2	121·5	119·0	116·9
N(10)–C(6)–C(5)	122·7	123·7	123·0	125·7
N(3)–C(4)–N(9)	128·3	127·4	127·1	128·4
C(6)–C(5)–N(7)	133·9	131·9	132·1	131·6
C(4)–C(5)–N(7)	110·7	112·3	111·0	111·2
C(5)–N(7)–C(8)	104·4	104·7	104·4	104·2
N(7)–C(8)–N(9)	113·2	111·8	112·9	112·0
C(8)–N(9)–C(4)	106·8	107·1	106·2	107·9
N(9)–C(4)–C(5)	104·8	104·1	105·5	104·7
†C(4)–N(9)–C(1′)	123·2	123·8	125·6	123·8
†C(8)–N(9)–C(1′)	129·6	128·6	128·2	128·3

* H Hoogsteen (1963)
KJ Kraut & Jensen (1963)
SJ Sundaralingam & Jensen (1963)
WST This investigation

† C(1′) only applies to WST and KJ; in the case of H and SJ, C(1′) is represented by the carbon atom of the methyl substituent, *i.e.*, C(11).

and 2-deoxy-D-ribofuranose. Recent evidence does not support this since angles C(2′)–C(3′)–O(3′) and O(3′)–C(3′)–C(4′) in deoxyadenosine and 5-fluoro-2′-deoxyuridine are significantly smaller than those for adenosine-5′-phosphate. This would suggest steric hindrance between O(2′) and O(3′) in D-ribofuranose resulting in larger exocyclic angles on C(3′) than those in 2-deoxy-D-ribofuranose. In cytidylic acid *b*, O(3′) is phosphorylated but a similar increase in exocyclic angles is observed for C(2′), in particular, angles C(1′)–C(2′)–O(2′) and O(2′)–C(2′)–C(3′). In addition to the relief of steric hindrance, deformation of the exocyclic angles may be a result of hydrogen bond formation.

Conformation of the molecule

The 'best' plane of the sugar residue, *i.e.* the plane through atoms C(1′), C(2′), C(4′) and O(1′), makes a dihedral angle of 69° with the adenine plane. This value is similar to those reported for other nucleosides and nucleotides.

As proposed by Donohue & Trueblood (1960), the conformation of the molecule can be described by the torsion angle φ_{CN} defined as the angle formed by the trace of the plane of the base with the projection of the C(1′)–O(1′) bond of the furanrose ring when viewed along the C–N glycosidic bond. Deoxyadenosine is in the *anti* conformation with $\varphi_{CN} = -3°$. All the nucleosides and nucleotides so far studied exist in the *anti* conformation but the angles φ_{CN} vary over a wide range, depending on the particular packing and hydrogen bond requirements.

Anisotropic vibration

The magnitudes and direction cosines of the principal axes of the ellipsoids of thermal vibration of the atoms are given in Table 10. The quantities C_{ia}, C_{ib} and C_{ic} are the cosines of the angles between the ith principal axis and the a, b and c axes of the unit cell. The B_i are quoted in Å^2. If one adopts the criterion for significant anisotropy that at least one of the β_{ij} (Table 2) for the atom should differ by more than 2σ from the value which it would have if the atom were vibrating isotropically with B equal to the mean principal axis B_i, then the thermal vibrations of C(2′) are not significantly anisotropic. If, on the other hand, the significance level is set at 3σ, atoms C(4), C(8), C(2′), C(3′) and O(1′) can be described as having isotropic thermal motion. If, instead of using the mean B_i value, one takes the isotropic B value obtained at the end of the isotropic least-squares analysis, the anisotropic vibrations of all atoms are significant at the 2σ level, whereas those for C(4), C(2′) and C(3′) are not, at the 3σ level. The direction cosines of the normal to the least-squares plane through the atoms of the purine residue with respect to the unit cell axes a, b and c are approximately $-0{\cdot}53$, $+0{\cdot}28$ and $-0{\cdot}83$ respectively. Inspection of Table 10 shows that, for the adenine residue, all atoms are vibrating with maximum amplitude in a direction approximately normal to the plane of the base. Of the remaining atoms, C(5′), O(3′), O(5′) and O(11) have the greatest freedom of movement, which is to be expected for the exocyclic atoms and the water molecule.

Table 9. *Comparison of bond distances and angles of the sugar residue in deoxyadenosine* (WST), *5-fluoro-2′-deoxyuridine* (HM), *calcium thymidylate* (THL), *adenosine-5′-phosphate* (KJ) *and cytidylic acid b* (SJ)*

N denotes the nitrogen atom of the glycosidic linkage.

	WST	HM	THL	KJ	SJ
C(1′)–C(2′)	1·509 Å	1·534 Å	1·527 Å	1·509 Å	1·513 Å
C(2′)–C(3′)	1·507	1·527	1·550	1·544	1·533
C(3′)–C(4′)	1·530	1·501	1·491	1·520	1·537
C(4′)–C(5′)	1·506	1·514	1·526	1·525	1·511
C(4′)–O(1′)	1·435	1·451	1·441	1·476	1·458
O(1′)–C(1′)	1·411	1·435	1·438	1·445	1·418
C(2′)–O(2′)				1·438	1·402
C(3′)–O(3′)	1·422	1·434	1·409	1·400	1·431
C(5′)–O(5′)	1·435	1·443	1·472	1·475	1·437
N–C(1′)–O(1′)	108·4°	107·3°	107·4°	107·2°	107·7°
N–C(1′)–C(2′)	110·5	113·6	115·0	112·6	112·9
O(1′)–C(1′)–C(2′)	107·3	104·7	107·2	106·7	105·9
C(1′)–C(2′)–C(3′)	103·3	100·4	103·3	101·7	100·8
C(1′)–C(2′)–O(2′)				107·0	114·6
O(2′)–C(2′)–C(3′)				110·0	118·1
C(2′)–C(3′)–C(4′)	101·5	102·1	101·8	99·9	102·2
C(2′)–C(3)′–O(3′)	107·7	108·6	114·3	115·4	108·1
O(3′)–C(3′)–C(4′)	111·3	112·3	113·7	115·5	110·0
C(3′)–C(4′)–C(5′)	113·7	114·6	117·1	119·1	116·0
C(3′)–C(4′)–O(1′)	104·9	106·3	106·7	104·0	104·7
C(5′)–C(4′)–O(1′)	112·2	108·4	107·6	107·9	110·0
C(4′)–O(1′)–C(1′)	109·9	109·2	108·9	108·3	110·3
C(4′)–C(5′)–O(5′)	107·1	106·5	109·4	107·6	113·6

* HM Harris & Macintyre (1964)
KJ Kraut & Jensen (1963)
SJ Sundaralingam & Jensen (1963)
THL Trueblood, Horn & Luzzati (1961)
WST This investigation

Table 10. *Magnitudes and direction cosines of the principal axes of the thermal vibration ellipsoids*

Atom	Axis i	B_i	C_{ia}	C_{ib}	C_{ic}
N(1)	1	4·82	0·485	0·009	0·819
	2	1·52	−0·812	0·376	0·529
	3	2·00	0·325	0·927	−0·223
C(2)	1	4·93	0·301	−0·261	0·880
	2	1·74	−0·624	−0·781	0·049
	3	2·19	0·721	−0·568	−0·472
N(3)	1	3·98	0·352	0·159	0·880
	2	0·99	−0·713	−0·594	0·447
	3	1·98	0·607	−0·789	−0·159
C(4)	1	1·11	−0·900	0·338	0·369
	2	2·48	0·361	0·224	0·862
	3	1·95	0·245	0·914	−0·347
C(5)	1	3·35	0·345	0·223	0·866
	2	1·26	−0·865	0·448	0·318
	3	1·78	0·356	0·866	−0·387
C(6)	1	0·82	−0·911	0·101	0·493
	2	3·61	0·412	0·184	0·844
	3	2·27	0·017	0·978	−0·210
N(7)	1	3·64	0·373	0·002	0·883
	2	1·39	−0·886	−0·295	0·449
	3	2·20	0·275	−0·955	−0·137
C(8)	1	3·06	0·316	−0·080	0·907
	2	1·68	−0·918	0·225	0·421
	3	2·09	0·239	0·971	−0·023

Table 10 (*cont.*)

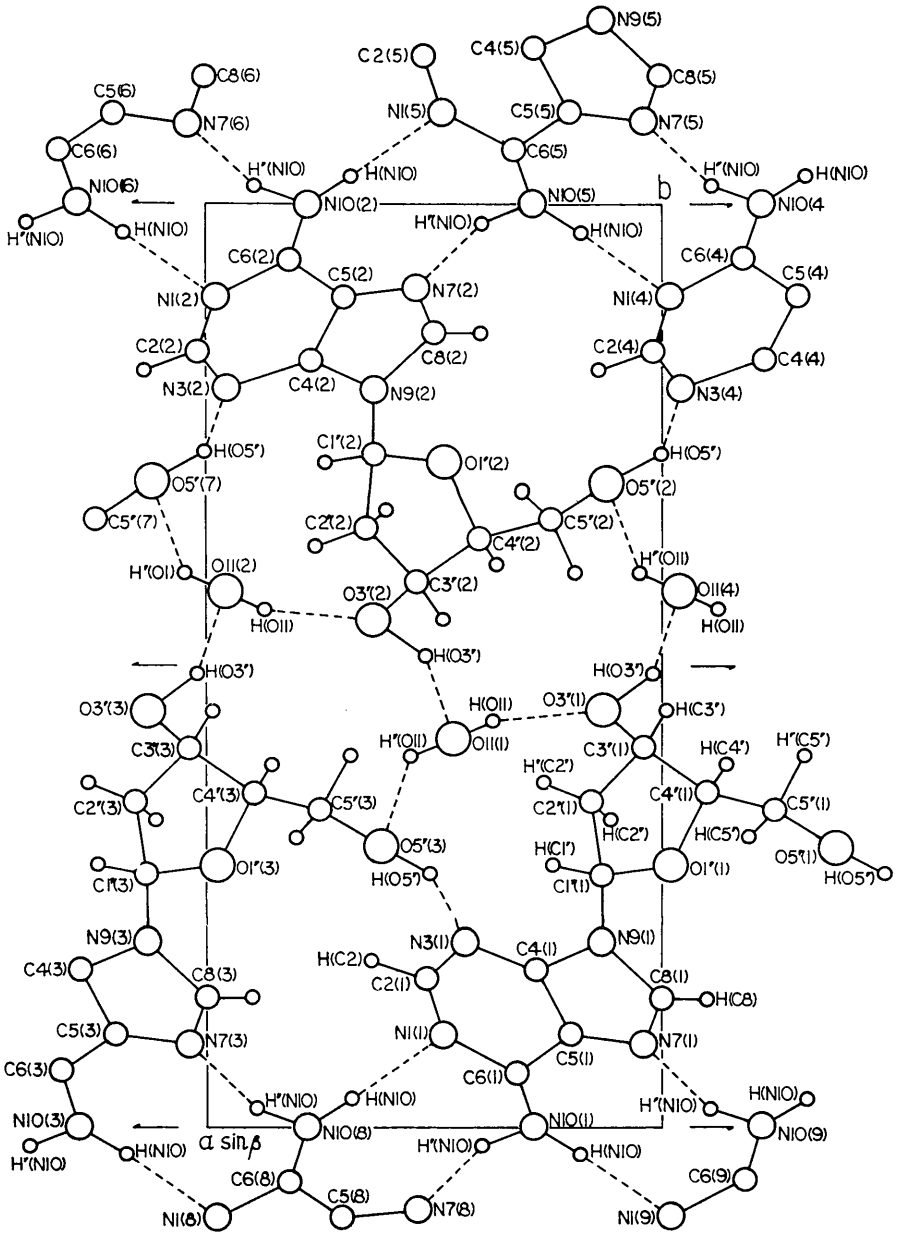

Fig. 7. Molecular packing viewed down the *c* axis.

Table 10 (*cont.*)

Atom	Axis *i*	B_i	C_{ia}	C_{ib}	C_{ic}
N(9)	1	2·93	0·396	−0·011	0·871
	2	1·45	−0·873	0·304	0·470
	3	1·87	0·283	0·953	−0·141
N(10)	1	5·27	0·496	−0·052	0·810
	2	0·97	−0·861	−0·159	0·571
	3	2·20	0·112	−0·986	−0·135
C(1′)	1	1·13	−0·861	0·051	0·594
	2	2·56	0·490	0·352	0·742
	3	2·30	−0·137	0·935	−0·311
C(2′)	1	2·91	0·410	−0·206	0·840
	2	1·93	−0·532	−0·845	0·106
	3	2·07	0·740	−0·494	−0·532
C(3′)	1	2·84	0·282	0·291	0·879
	2	1·25	−0·666	−0·627	0·473
	3	2·01	0·691	−0·723	−0·056
C(4′)	1	2·91	0·289	0·206	0·899
	2	1·10	−0·883	0·435	0·269
	3	1·63	0·371	0·876	−0·345

Table 10 (*cont.*)

Atom	Axis *i*	B_i	C_{ia}	C_{ib}	C_{ic}
C(5′)	1	3·90	0·483	0·029	0·819
	2	1·46	−0·552	−0·766	0·387
	3	2·42	0·680	−0·643	−0·424
O(1′)	1	1·31	−0·772	0·489	0·485
	2	2·82	−0·047	−0·682	0·731
	3	2·20	−0·634	−0·545	−0·479
O(3′)	1	4·75	0·330	0·159	0·890
	2	1·03	−0·829	−0·423	0·452
	3	2·17	0·452	−0·892	−0·056
O(5′)	1	5·75	0·625	−0·337	0·634
	2	1·31	−0·631	−0·750	0·266
	3	2·74	0·460	−0·570	−0·726
O(11)	1	7·30	0·489	0·098	0·810
	2	1·53	−0·780	−0·396	0·565
	3	2·33	0·391	−0·913	−0·158

Table 11. *The intermolecular distances less than* 4 Å

The second of the two numbers in parentheses in each case indicates the atomic position as follows:

(1) x, y, z
(2) $1-x, y-\frac{1}{2}, 1-z$
(3) $x, y-1, z$
(4) $1-x, y+\frac{1}{2}, 1-z$
(5) $x-1, y, 2+z$
(6) $x-1, y-1, 2+z$
(7) $1-x, y-\frac{3}{2}, 1-z$
(8) $2-x, y-\frac{1}{2}, -1-z$
(9) $2-x, y+\frac{1}{2}, -1-z$
(10) $x, y, 1+z$
(11) $x, y+1, z$

N(1)(1)–C(6)(8)	3·944 Å
N(1)(1)–N(7)(8)	3·884
N(1)(1)–N(10)(8)	2·877
C(2)(1)–N(10)(8)	3·518
C(2)(1)–C(5′)(3)	3·909
C(2)(1)–O(5′)(3)	3·494
N(3)(1)–N(1)(10)	3·508
N(3)(1)–C(2)(10)	3·947
N(3)(1)–C(6)(10)	3·893
N(3)(1)–C(5′)(3)	3·556
N(3)(1)–O(5′)(3)	2·775
C(4)(1)–N(1)(10)	3·621
C(4)(1)–C(6)(10)	3·515
C(4)(1)–N(10)(10)	3·552
C(4)(1)–O(5′)(3)	3·842
C(5)(1)–C(6)(10)	3·970
C(5)(1)–N(10)(9)	3·991
C(5)(1)–N(10)(10)	3·513
C(6)(1)–N(7)(8)	3·919
C(6)(1)–N(10)(8)	3·806
N(7)(1)–N(10)(9)	3·033
N(7)(1)–N(10)(10)	3·637
C(8)(1)–C(5)(10)	3·891
C(8)(1)–C(6)(10)	3·836
C(8)(1)–N(7)(10)	3·899
C(8)(1)–N(10)(9)	3·942
C(8)(1)–N(10)(10)	3·678
N(9)(1)–N(1)(10)	3·876
N(9)(1)–C(5)(10)	3·581
N(9)(1)–N(7)(10)	3·981
N(9)(1)–N(10)(10)	3·689
N(9)(1)–C(6)(10)	3·462
N(10)(1)–N(10)(9)	3·936 Å
C(1′)(1)–C(4)(10)	3·720
C(1′)(1)–C(5)(10)	3·684
C(1′)(1)–C(6)(10)	3·948
C(1′)(1)–C(2′)(10)	3·988
C(1′)(1)–O(5′)(3)	3·843
C(1′)(1)–O(11)(1)	3·822
C(2′)(1)–O(5′)(3)	3·916
C(2′)(1)–O(11)(1)	3·674
C(3′)(1)–O(11)(1)	3·796
C(3′)(1)–O(11)(4)	3·388
C(4′)(1)–C(5′)(10)	3·923
C(4′)(1)–O(11)(4)	3·868
C(4′)(1)–O(11)(11)	3·803
C(5′)(1)–O(11)(11)	3·426
O(1′)(1)–C(4)(10)	3·795
O(1′)(1)–C(5)(10)	3·765
O(1′)(1)–N(7)(10)	3·706
O(1′)(1)–C(8)(10)	3·664
O(1′)(1)–N(9)(10)	3·689
O(1′)(1)–C(2′)(10)	3·561
O(1′)(1)–C(5′)(10)	3·967
O(3′)(1)–C(2′)(10)	3·412
O(3′)(1)–C(3′)(10)	3·786
O(3′)(1)–O(11)(1)	2·733
O(3′)(1)–O(11)(4)	2·649
O(5′)(1)–O(11)(11)	2·763
O(11)(1)–N(3)(10)	3·823

The molecular packing and hydrogen bonding

The tendency of the pyrimidine and purine bases to pack in parallel planes about 3·5 Å apart and their preference for hydrogen bonding among themselves is well exemplified in deoxyadenosine. The packing in the crystal involves direct base linkages between molecules rather than the formation of hydrogen bonds between sugars or water molecules and bases. The mode of packing and hydrogen bonding is displayed in Fig. 7 and the shortest intermolecular contacts not involving hydrogen atoms are listed in Table 11.

In deoxyadenosine there are infinite chains of N–H · · · N bonds of length 2·88 and 3·03 Å linking each NH_2 group with N(1) and N(7) respectively in the molecules above and below and related to the reference molecule containing the NH_2 group by the screw axis. The bases lie almost in the (201) plane ($d_{201}=3{\cdot}86$ Å) and the spacing between parallel adenine groups is 3·67 Å. The water molecule forms three O–H · · · O bonds, with O(3′) in the reference molecule at x, y, z (2·73 Å), O(3′) at $1-x$, $-\frac{1}{2}+y$, $1-z$ (2·65 Å) and O(5′) at x, $-1+y$, z (2·76 Å). The atom O(5′) also forms a hydrogen bond of length 2·78 Å with N(3) in the molecule at x, $y+1$, z. The angles O(3′)(1)–O(11)(1)–O(3′)(2), O(3′)(2)–O(11)(1)–O(5′)(3) and O(5′)(3)–O(11)(1)–(O3′)(1) are 118·5, 120·3 and 111·9° respectively (see Table 11 for the meaning of numbers in the second parentheses). The atom O(11)(1) is displaced from the plane defined by O(3′)(1), O(3′)(2) and O(5′)(3) by 0·49 Å. Thus the hydrogen bonds formed by the water molecule may be described as distorted trigonal Threefold and almost planar hydrogen-bond coordination of water molecules has been reported in the structures of cytosine monohydrate (Jeffrey & Kinoshita, 1963) and barbituric acid dihydrate (Jeffrey, Ghose & Warwicker, 1961).

In view of the very high standard deviations in distances and angles involving hydrogen atoms, no attempt is made to discuss the deviations from linearity of the hydrogen bonds.

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